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A NEW SPECIES OF TYPHLOPLANA (RHABDOCOELE TURBELLARIA)  
AND SOME ADDITIONAL DATA CONCERNING MESOSTOMUM  
VIVIPARUM (SILLIMAN) FROM NORTHERN INDIA

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1. INTRODUCTION.

The earliest record of investigation of Typhloplana (Rhabdocoela) is of more than one hundred and forty years old. Muller (1774) gave an account of *Rhynchomesostoma rostratum*, Abildgard (1789) described *Typhloplana viridata* and since then allied freshwater Turbellarians have been carefully worked out by a large number of distinguished workers. In America the first description of the common planarian was given by Leidy<sup>23</sup> (1848). The Indian species of Rhabdocoela Turbellarians, however, have received little attention and no description of any species of Typhloplana from India seems to exist. This communication provides an account of a new species of the genus Typhloplana *T. vitellata* sp. n. found in freshwater lakes and ponds near the river Ganges in Allahabad and records a few observations on the structure of *Mesostomum viviparum* from pools near the same river in Benares. These Turbellarians show certain peculiarities in structure and habits of life which make them particularly interesting.

The work was carried on in the Zoology Department of the University of Allahabad. The author wishes to express his sincere thanks to Professor D. R. Bhattacharya, for advice and kind criticism, and to Dr. H. R. Mehra and Mr. S. C. Verma for material and help in the correction of manuscript.

2. METHODS AND TECHNIQUE.

Samples of surface water from different parts of the pond were taken in jugs with a quantity of algae and weeds and brought to the laboratory for examination. Sometimes only the algae and weeds were taken up and placed in a jar with a small amount of water. The bottom-mud was also scraped up, but this contained mostly aquatic oligochaetes. Glass basins 11" broad and 7" high served for aquaria in which the flow of water was maintained by means of water taps. The

collections were made periodically from August to April, for two years, from pools of water artificially cut off from main stream of the Ganges by embankments. One pool near Bund Road in which the water remained comparatively less agitated by cattle provided the most sure and plentiful material. In this pond *Spirogyra*, *Nostoc*, and other algae were quite profuse and hence regular oxygen supply was assured—a condition very favourable for the *Rhabdocoele Turbellaria*, which though found throughout the winter months were particularly abundant in March and April.

Isolated specimens were kept alive for several days in a watch glass, some of them lived for nine to twelve days during the month of December at room temperature. But in April when the days are fairly warm they die soon. The water in the watch glass, however, was not artificially aerated, but was changed every morning and evening.

The worms are so delicate that even the pressure of a cover glass is sufficient to crush them. They are, however, studied in the living condition by putting *spirogyra* filaments under the cover glass. In order to check the movements of the worm drops of 10% chloretone were dropped underneath the cover glass gently and with great care as otherwise, the integument is liable to get ruptured.

For permanent preparation specimens were narcotised by a fairly large dose of 10% chloretone which was added little by little until they expanded. Warm saturated solution of corrosive sublimate in physiological salt solution and hot Zenker's fluid without acetic were used for fixation. Acetic acid as far as possible should not be used in the fixative as it readily brings about a rupture of the integument. The anaesthetic was not used in the case of worms fixed in Zenker's solution. The specimens from Benares were fixed in Flemming's fluid without acetic and Champy's solution. For toto preparations materials fixed in corrosive sublimate solution and stained with Borax carmine gave good results. The sections were stained with Iron Haematoxylin or Borax carmine and Picro Indigo carmine.

### 3. HABITS OF LIFE.

Some observations were made on the habits of life of the worms and their reaction to external stimuli and poisons. In a jug full of pond water and algae, allowed to stand overnight, it was seen that almost all the individuals had left their hiding places and come to lie near the surface, and in this condition they can be easily collected either by means of a pipette or by draining out the surface water of the jug in another glass basin.

It appears that they react negatively to the stimulus of light avoiding the sunlight as much as possible and habitually living in dark shady places among large clumps of aquatic plants and masses of algae.

The reaction displayed by the worms to anaesthetising agents and poisons is interesting. Although they are very delicate in structure, they appear to offer a remarkable resistance to anaesthetics and poisons. A comparatively large dose (added very gently drop by drop) is necessary to narcotise them. The following (table 1) shows the relative reaction of four different poisons on the flatworm:—

Table 1

| No of worms in<br>10 c. c. of pure<br>water. | Chloral hydrate<br>10 per cent. | Chloretone<br>10 per cent. | Alcohol<br>90 per cent. | Tobacco extract<br>(strong). |
|--|---------------------------------|----------------------------|-------------------------|------------------------------|
| 5  | 1.5 c.c.                        | 1 c.c.                     | 1.5 c.c.                | 3 c.c.                       |
| 8  | 1.7 c.c.                        | 1.5 c.c.                   | 2.1 c.c.                | 4.2 c.c.                     |
| 10   | 1.8 c.c.                        | 1.8 c.c.                   | 2.5 c.c.                | 5 c.c.                       |
| 12   | 2 c.c.                          | 2.1 c.c.                   | 2.6 c.c.                | 5.5 c.c.                     |

#### 4. MORPHOLOGY OF *TYPHLOPLANA VITELLATA* N. Sp.

*T. vitellata* are gregarious, occurring in large numbers particularly in the months of March and April. The colour is white and appears to remain so constantly, while in most Rhabdocoeles it is dull and varying. The worms are extremely delicate and unable to withstand even the light pressure of a cover glass. The size of living specimens (Fig. 1) varies 1 mm. to 1.8 mm. in length and from 0.2 mm to 0.5 mm in breadth. Apparently all individuals observed were sexually mature. Fixed specimens (Fig. 2) measured 0.8 mm. to 1 mm. in length and 0.1 mm. to 0.3 mm. in breadth. The variation in size depended also upon the amount of food swallowed and the degree of development of the reproductive organs.

The surface of the body is covered with a coat of cilia by the movements of which the worm glides gracefully on the slide. The cilia also enable the animal to propel its body through entanglements of algae and weeds in the aquarium. The body is elongated and cylindrical but not very flat. The anterior end is bluntly pointed and can be drawn in, to a slight extent, on contraction (Fig. 2, PRB). A pair of eye spots is situated on the dorsal side a little behind the anterior extremity. The posterior one-fourth of the body narrows back rapidly to a pointed tip. The mouth is situated on the ventral side at about one-fourth body length from the anterior end. The genital aperture (Fig. 3 GP) lies immediately behind the pharynx. The eggs are brown and visible through the transparent skin.

*Epithelium.* The integument is composed of a single layer of columnar epithelial cells ciliated on the outside. The cilia are extremely fine and visible

under the high power only. The cells contain small spindle-shaped rhabdites (Fig. 7, RBD) lying either singly or in pairs, which are scattered all over and not localised to any particular part of the body. Underlying the columnar epithelium lies a very thin basement membrane with which is connected a thin layer of muscle fibres. The average thickness of the integument is  $6\mu$ .

*The Muscular System.* The musculature is feebly developed in the body-wall. It consists of fine fibres running in all directions to form a sort of mesh-work just beneath the basement membrane. It is better developed towards the anterior end where a bundle of threadlike strands of muscles connects the extremity with the parts behind (Figs. 3 & 5, PRBM). The fibres in this bundle are long and arranged in antero-posterior or oblique direction helping the animal to retract or protrude its anterior end, which is the most sensitive part of the body.

The pharynx is thick and muscular and worked by muscle fibres connecting it with the ventral body wall. The intrinsic muscles of the pharynx are thick, stout bands running on the outer and inner edges of the bulb. There are also a few concentric sphincter muscle bands on the outer margin of the bulb rendering the pharynx an efficient suctorial organ.

The cirrus is muscular and lies in the neighbourhood of the pharyngeal bulb (Fig. 4, CIR). There is a distinct atrium; the atrial pore is provided with a sphincter muscle. Bands of muscle fibres connect the cirrus to the body wall evidently to control its protrusion and retraction.

*Parenchyma.* The parenchyma or mesenchyma is composed of irregular vacuolated cells (Figs. 3, 5, 6, PAR) of very variable forms (spherical, ovoidal or angular) lying in the interstices between the organs. The parenchyma cells are subject to compression and strain. When the intestine is choked with food the cells appear to be squeezed out of existence. On the other hand when the digestive cavity is empty the lumen of the intestine is almost obliterated and the whole body seems to be made up of parenchyma alone. The cells also conduct food and oxygen to different parts of the body through the intermediation of the fluid in the vacuoles which act as a sort of water vascular system.

*Digestive System.* The mouth is situated on the ventral side, in the anterior third of the body, and leads into a powerful muscular pharynx (Fig. 4, PHR) which bears rosette-shaped spines at the internal end. The pharynx opens into a simple sac-like intestine which extends antero-posteriorly. The wall of the intestine is not very clearly distinguishable when there is no food in the intestine as it is pressed considerably by the parenchyma and surrounding organs. Unlike many Rhabdocoela, which generally live on dead organs, *Typhloplana vitellata* seems to be carnivorous feeding upon small living aquatic oligochaetes. It is an aggressive species, which was found on many occasions to attack in numbers the Naids and other aquatic oligochaetes breaking their body into pieces with the powerful pharynx.



*Nervous System.* The nervous system is diffuse and not sharply marked off into nerve centres. The nerve cells and fibres are almost undifferentiated from the general tissues of the body. There is hardly any indication of nerve swellings to form a definite cerebral ganglion, at the anterior end. The nerve fibres are, however, much more concentrated between the two eye spots than elsewhere in the body to form the brain. The nerve fibres are also distributed over the general surface of the skin.

*Sense Organs.* The two eyes are the only sensory organs (Fig. 1) which lie anteriorly, on each side of the median line, dorsal to the brain beneath the epithelium. Each is a simple aggregation of dark, coarse pigment granules, surrounded by cells which are supplied directly with nerve fibres from the brain.

*Reproductive System.* The reproductive organs consist of two tubular testes, one ovary, four lobes of vitelline glands and a cirrus (Fig. 4, CIR). The genital opening is single and lies ventrally in the middle line close to the pharynx. The testes are elongated structures situated ventral to the intestine. Their ducts are short and lead to the cirrus. The cirrus is an ovoidal muscular organ about one-third the diameter of the pharynx measuring  $40\mu$ – $50\mu$  in greatest diameter.

The ovary is a small spherical body lying close to the pharynx. During the spring when a large number of isolated eggs are found in the body, it becomes greatly shrunk. The eggs, 20–30 in number nearly fill the whole of the interior of the body—some crowded towards the head, others lying in the middle and the posterior regions. Most of the eggs have a very thick shell of dark brown colour. Those are probably winter eggs. Others which are probably newly formed have a thin transparent shell. The size of the eggs varies from  $50\mu$ – $130\mu$  in diameter. The vitelline glands of a characteristic shape are composed of four groups of compact follicles, which are situated ventral to the intestine. During the sexual period they grow to a large size but towards the close of the spring they shrink very much to make room for the fully grown eggs. The eggs are shed to the exterior either through the genital pore or frequently through a temporary rupture, in the body wall, at any place. Although a large number of specimens were examined regeneration was not observed in any case. Occasionally I met with an individual filled with ova becoming inactive and breaking its dorsal body-wall to discharge the eggs. The rupture did not heal and the worm consequently perished.

Attempts were made to study the stages in the development of the worm but all the extruded eggs kept for the purpose disintegrated before long.

*Excretory System.* The excretory tubules can be seen faintly in living specimens. There are two longitudinal tubules on either side, running along the margin, throughout the whole length of the body. A little in front of the pharynx, the two lateral tubules give out two tiny branches which approach each other forming a loop ventrally and open to the exterior by a median canal near the edge of the pharynx.

The genus *Typhloplana*, as it now stands, comprises only two species:—*T. marinus* Oersted and *T. viridata* Abildgard of which only the latter is a freshwater form. The following (table 2) giving characteristic features of *T. viridata* and *T. vitellata* indicates the marked differences between these species. *T. marinus* being a marine species is not included in the table for comparison.

Table 2

| Characters.          | <i>T. viridata</i> . Abild., 1789.   | <i>T. vitellata</i> . N. Sp.  |
|----------------------|--|---|
| Habitat ...          | Freshwater ...   | Freshwater.   |
| Length ...           | 0.5—1 mm. ...  | 1.0—1.8 mm.   |
| Anterior end ...     | The anterior end is contractile, the amount of contraction is much less.   | The anterior end is very much contractile.  |
| Colour ...           | The presence of zoochlorellae imparts the colour which varies from pale gray-green to brilliant green.                   | The colour is cream-white. No symbiotic algae observable.   |
| Rhabdites ...        | Rhabdites are small 8-9 $\mu$ cylindrical rods with round blunt ends, lie in the parenchyma just beneath the epithelium. | Rhabdites are much smaller 3-4 $\mu$ spindle-shaped, pointed at both ends, lie in the epithelium. |
| Genital pore ...     | Posterior to the pharynx guarded by a broad band of circular muscles.  | Posterior to the pharynx-rosette, near the edge, guarded by a sphincter muscle.                   |
| Testes ...           | Two large solid lobes ventral to the intestine   | Two lobes of testes ventral to the intestine.   |
| Cirrus ...           | Cirrus large, nearly as large as the pharynx.  | Cirrus small, about $\frac{1}{3}$ the size of the pharynx.  |
| Ovary ...            | Single ...   | Single. Situated near the Pharynx.  |
| Vitelline glands ... | Two lobes ...  | Four lobes.   |
| Eggs ...             | 90—100 ...   | 80 $\mu$  |

The two species are distinguished from each other here in the following respects:—

1. Colouration.
2. Size of the body.
3. Shape of the anterior end.
4. Size and form of the vitelline glands and cirrus.
5. Dimensions of the rhabdites.

5. MESOSTOMA (*TYPHLOPLANA*) VIVIPARUM SILLIMAN

Silliman<sup>35</sup> described this species from lakes of North America under the name of *Mesostoma viviparum*. Luther<sup>25</sup> and Von Graff<sup>15</sup> considered it as identical with the European species, *Typhloplana viviparum*.

The writer had an opportunity of examining some specimens of *Mesostoma* (*Typhloplana*) *viviparum* collected by Dr. H. R. Mehra, in 1924 from a pond, near Benares (North India). The specimens resembled in many respects the European and American types.

The worms in the fixed condition measured 2.0–2.5 mm. in length and 1.0 mm. in breadth. The head and the tail are not pointed but they are somewhat blunt. The rhabdites (Fig. 8, RBD) are spindle-shaped. The intestine appears only as a chink in the parenchyma (Fig. 9, S. I.), no distinct layer of epithelium surrounding the intestine is visible in any of the sections cut by me. The pharynx is a spherical rosette-shaped structure which is seen fairly well developed even in the embryos contained within the uterus.

The reproductive organs (Fig. 10) are complicated and difficult to make out. The ovaries and the testes are not clearly visible as the worms were probably not collected in the breeding season. The vetelline glands consist of two elongated follicles lying laterally to the intestine. The most interesting feature, as already observed by previous workers, is the viviparous habit. The young ones are developed in a special brood pouch which is an outgrowth of the uterus lying on the dorsal side of the intestine (Fig. 9, EMB). There are usually two to four embryos occupying the uterus.

## 6. CLASSIFICATION.

The first systematic classification of the Rhabdocoele Turbellarians was given by Ehrenberg<sup>11</sup> (1831–36). He established the genus *Typhloplana* in 1831 and five years later in 1836 created the family Mesostomidae to include a large number of genera—*Eumesostomum*, *Mesostomum*, *Typhloplana* etc. In 1852 Leuckart<sup>24</sup> published his monograph on *Mesostomum ehrenbergi* and retained the family name Mesostomidae. Von Graff<sup>15</sup> in his memorable work “Monographie der Turbellarian Rhabdocoelida” published in 1882, maintained eight species of *Typhloplana* six of which he regarded synonymous as follows:—

*Mesostomum sulphurium* De Mann = *Typhloplana sulphurium* O. Schmidt.

*Monotus lineatus* Diesing (Alloiocoela) = *Typhloplana flustrae* Johnston.

*Mesostoma gracialis* Mihi = *Typhloplana gracialis* Schmarda.

*Mesostoma herudo* O. Schmidt = *Typhloplana herudo* Diesing.

*Mesostoma griseum* Mihi = *Typhloplana flava* Ehrenberg.

*Derostoma flava* Graff (Vorticidae) = *Typhloplana variabilis* Oersted.

Subsequently, however, in 1905, he himself split up the family Mesostomidae by removing the genera *Typhloplana* and *Eumesostomum* into a separate family called

*Typhloplanidae*. He retained *T. viridata* and *T. marinus* in the genus *Typhloplana* and relegated the six abovementioned species to other genera. This system of classification remained in practice until Poche<sup>29</sup> (1925) propounded his elaborate scheme in which the order Rhabdocoela is broken up into twenty-one families.

A chart giving the diagnostic characters of the families and genera of the freshwater Rhabdocoela is appended.

#### 7. SUMMARY

The anatomy of a new Rhabdocoele Turbellarian (*Typhloplana vitellata*) is described and its differences with other species of the genus are pointed out.

The bionomics of the new species is given and its food, mode of locomotion, response to light and reaction to narcotics are considered.

Some additional data regarding *Mesostoma viviparum* Silliman are provided based on the study of the Indian specimens.

A brief history of the genus *Typhloplana* is furnished and a scheme for the diagnosis of the family and genera of the order Rhabdocoela is provided in the appendix.

APPENDIX

**Diagnostic Key to the Families, and Genera of the Order Rhabdocoela.\***

GROUP (A)—*Pharynx: simple.*

Reproductive organs simple. Female organ consists of ovary only; no uterus, no female copulatory apparatus, etc. Asexual reproduction is found to exist.

Order Rhabdocoela Ehrenberg, 1831.

Intestine—A simple blind tube.

Pharynx.—Simple, cask-shaped or rosette-shaped, or long cylindrical bulbous.

Connective tissue of the body-cavity poorly developed. The parenchyma consists of a few strands of connective tissue with large spaces filled with fluid.

GROUP (B)—*Pharynx: rosette-shaped, or cask-shaped.*

Situated perpendicular to the ventral surface or slightly inclined.

GROUP (C)—*Pharynx: long cylindrical bulbous.*

Without statocyst or preoral circular groove, with ciliated pits.  
Genus *Catenula*.

Ciliated pits well developed without proboscis.  
Genus *Stenostomum*. O. Schm.

Family *Catenulidae* Graff, 1905.  
Protonephridium with *one* principal branch; median dorsal in position.

Ciliated pits shallow, clubshaped, proboscis is present.  
Genus *Rhynchoscolex*.

(A) *Pharynx: simple, etc.*

Pharynx opens into anterior end of the intestine which has short diverticula.  
Genus *Macrostomum*. E.V.B.

Family *Microstomidae* Hallez, 1894  
Protonephridium with *two* lateral branches.

Mouth on the ventral surface, intestine extends dorsally and anteriorly beyond the pharynx. Testes and ovary either paired or unpaired. Two sexual apertures ventrally disposed, male posterior to the female. With or without eyes.  
Genus *Microstomum*. O. Schm.

\* For details of classification, the works of Graff<sup>15</sup> Poche<sup>29</sup> Steinmann and Bresslau<sup>40</sup> and several others mentioned in the Bibliography may be consulted.

- Family Graffillidae, Graff, 1908.  
Pharynx pyriform or with a barrel-like structure.  
Reproductive organs:—The female genitalia consists of either a paired or unpaired germ-vitellaria or with a pair of germaria and vitellaria. Parasitic in habit.
- With a unpaired germ-vitellaria.  
Genus Archivortex silvestris
- Reis. With paired germ-vitellaria or germaria and vitellaria.  
Genus Vejlovskya Graff—marine.  
Genus Anoplodium Schneider.  
Parasitic in Gastropoda (mollusc)  
Genus Fecampia Giard. in Decapod crustacea.  
Genus Graffilla Jher. in Gastropoda.  
Genus Syndesmis Silliman. in Echinoids.
- Family Dalyellidae, Graff 1905.  
Pharynx cask-shaped parallel to the ventral surface or slightly inclined with the end directed forward with only one genital pore.
- Sexual pore anteriorly situated, Yolk glands network or much branched Genus Dalyellia Fleming 1882.  
Genus Phaenocora Ehrenberg, 1836.
- With a separate pocket for chitinous portion of the male copulatory organ.  
Genus Jensenia Silliman, 1885.
- Family Gytracidae Ehrenberg, 1831.  
Pharynx rosette, situated a little anterior to the middle.  
Reproductive organs:—Vitelline glands large and ovary small. Two genital pores instead of one Proboscis bearing Rhabdocoels.
- Ovary lying in the centre, testes dorsal to the intestine.  
Genus Gytratrix. Ehrb.  
Genus Schizorhynchus. Hallez  
Genus Polycestus.
- (B) *Pharynx: rosette-shaped or cask-shaped, etc.*
- Family Mesostomidae Ehrenberg, 1836. Pharynx rosette, situated in the middle of the body. Vitellaria follicular. Genital pore behind the mouth.
- With one genital pore Genus Mesostomum M. Ehrenbergii Focke, 1836.  
M. angulare Higl. With two genital pores, male anterior to female  
Genus Byrsophlebs Jensen.  
Genus Proxenetes Jensen.
- Tribe Protoplanellini Reisinger, 1923. Genital pore in the posterior third of the body. Vitellaria situated ventral to the testes and separated from the opening of the excretory duct. Genera Protoplanella, Olisthanellinella, etc., etc.  
Reisinger, 1923 (30) (see Zool. Anz.)

Family Typhloplanidae Graff  
1905.

Pharynx rosette-shaped standing  
perpendicularly to the ventral  
surface.

Tribe Typhloplanini Reis 1923.

Genital pore in anterior two-  
third of the body. Vitellaria  
ventral to the testes. Testes not  
very far separated from the  
excretory pore.

Genera:—

Macrophysalophora Reis, 1923.

Adenoplea . . . . . [see Reisinger  
(30) Rhynchomesostoma Muller.

Anterior end of the body a re-  
tractile proboscis, body fluid red  
or yellowish-red, intestine con-  
tains orange oil drops. Strongy-  
lostoma Silliman, 1885. Without  
proboscis and atrial copulatory  
apparatus. With separate  
receptaculum seminis.

Genus Typhloplana.

T. Viridata Abild.

T. Vitellata n. sp.

Pharynx just anterior to the centre.  
Sexual pore close behind the  
pharynx. Without receptaculum  
seminis. Zoochlorellæ imparts  
green colour to the body in T.  
viridata. Tapering at both ends.  
Anterior end slightly retractile.

Reproductive organs:—

Genital pore behind the mouths

Ovary single, Testes paired.

Excretory tubes with two main  
branches which may have  
either one or two openings on  
the ventral surface or may lead  
to the mouth or sexual pore.

Ciliated pits may or may not be  
present.

Rhabdites play important part  
in classification.

(B) *Pharynx rosette-shaped  
or cask-shaped, etc.,  
(contd).*

Family Prorhynchidae Diesing

Without accessory female copula-  
tory organ. Male pore opens  
in common with the pharynx.  
Ovary single germvitellarium.  
Pharynx long.

Genus Prorhynchus. M. Schm.

(C) *Pharynx long cylin-  
drical bulbous.*

Family Solenopharyngidae Carus.  
With accessory female copulatory  
organs.

Pharynx cylindrical bulb-like.

Genus Solenopharynx. V. Gr.

Family Acanthopharyngidae  
Pharynx bulbous (Reis).

Genus Acanthopharynx Reis.

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#### EXPLANATION OF FIGURES

(*Typhloplana vitellata*, Figs. 1-7. *Mesostomum viviparum*, Figs. 8-10. All figures have been drawn under camera lucida.)

- Fig. 1.—Dorsal and ventral aspects of living specimens. The pharynx rosette is seen on the ventral side. Here and there are eggs with orange-red shell wall. The eye spots are situated dorsally at the anterior end.
- Fig. 2.—Five mounted specimens under low power. The eggs are grouped at the centre. The anterior tip is retracted in all the specimens.
- Fig. 3.—Entire mount showing general anatomy. The vitellaria are four-lobed. The ovary is single.
- Fig. 4.—Diagrammatic representation from life showing genital opening and pharynx.
- Fig. 5.—A median longitudinal section showing internal anatomy.
- Fig. 6.—Transverse section through the retracted anterior end.
- Fig. 7.—Transverse section of the integument showing epithelium with rhabdites.

Fig. 8.—Transverse section of the integument showing epithelium with rhabdite (M. viviparum.)

Fig. 9.—A median longitudinal section showing embryos in uterus.

Fig. 10.—Part of the above highly magnified showing genital opening and pharynx.

#### LETTERING

CIR.—Cirrus.

EMB.—Embryo.

EG.—Egg with thick brown shell.

EP.—Integumentary epithelium.

GER.—Germarium.

GP.—Genital pore.

PAR.—Parenchyma.

PHE.—Pharynx of the embryo.

PHR.—Pharynx rosette

PRB.—Proboscis. (Retractable anterior end.)

PRBM.—Proboscis muscle.

RBD.—Rhabdite.

SI.—Intestinal space.

SV.—Seminal vesicle.

T.—Testes.

VIT.—Vitelline gland.

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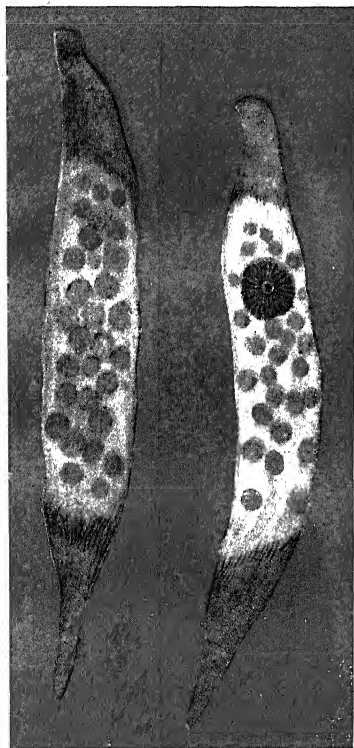


Fig. 1

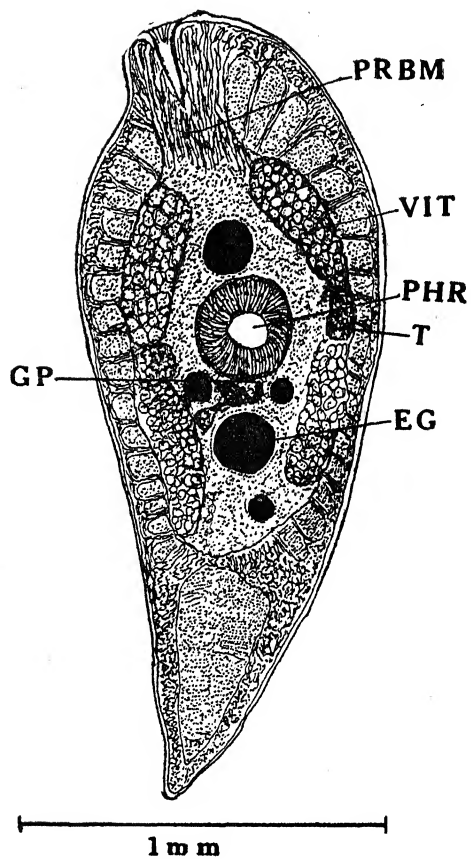


Fig. 3

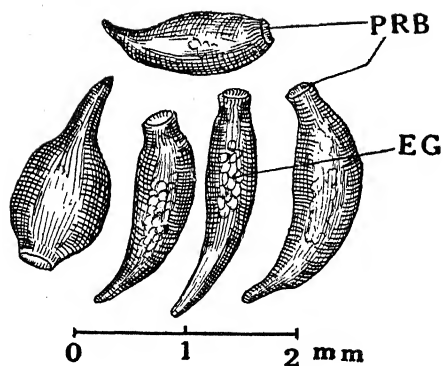


Fig. 2

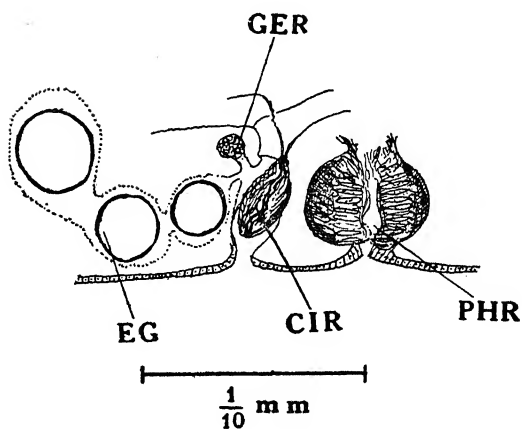


Fig. 4

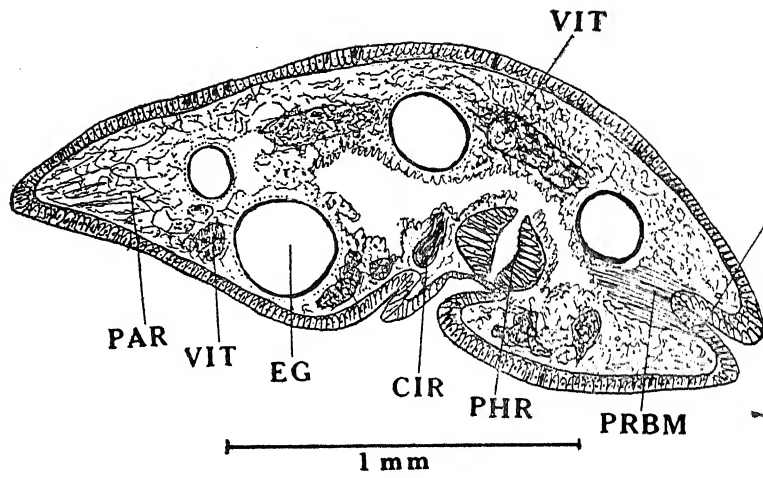


Fig. 5

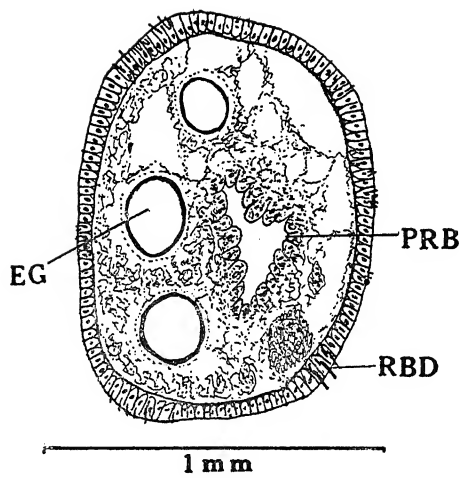


Fig. 6

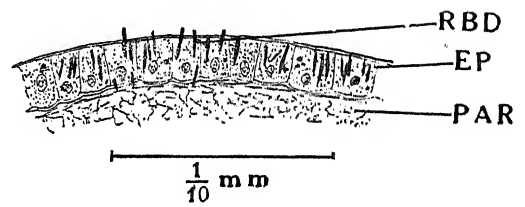


Fig. 7

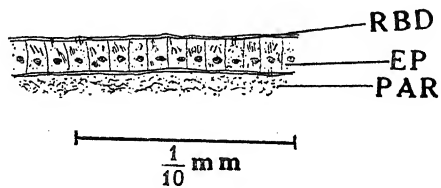


Fig. 8

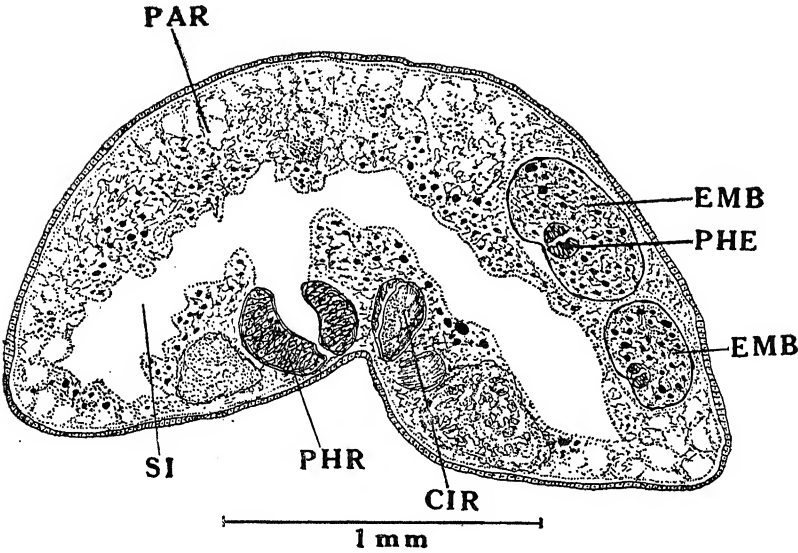


Fig. 9

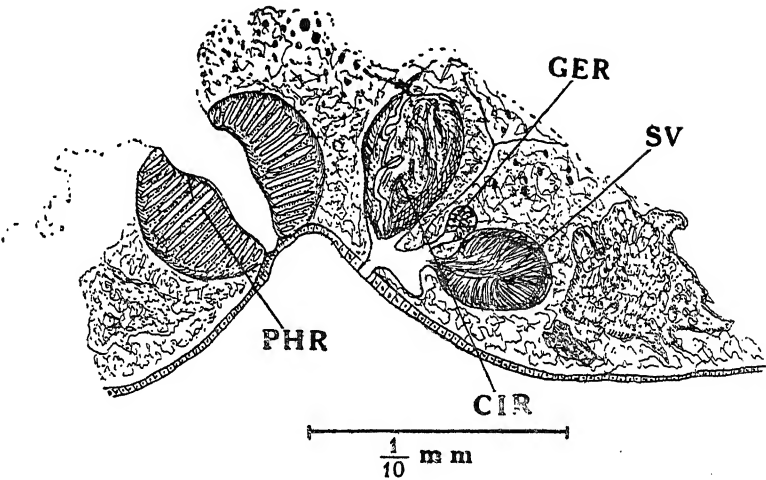


Fig. 10

# ON THE EXISTENCE OF A METRIC AND THE INVERSE VARIATIONAL PROBLEM

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1. An extension of Riemannian Geometry begins with the postulation of existence of  $n^3$  functions of position  $\Gamma_{jk}^i$  which are transformed by the point transformation ( $x \leftrightarrow x'$ ) in the following manner :

$$(1.1) \quad \Gamma_{jk}^i = \Gamma_{mn}^r \frac{\partial x'^i}{\partial x^r} \frac{\partial x^m}{\partial x'^j} \frac{\partial x^n}{\partial x'^k} + \frac{\partial x'^i}{\partial x^r} \frac{\partial^2 x^r}{\partial x'^j \partial x'^k}$$

We here adopt the following notation:—

(a) The "dummy index" occurring both as subscript and superscript indicates summation over all values.

$$A_r u^r = A_1 u^1 + A_2 u^2 + \dots + A_n u^n$$

(b) But when underlined, the summation is not to take place ; also, indices on the same level with a bar over them are to be summed :

$$A_{\underline{r}} u^{\underline{r}} = \text{the } r\text{th term in } A_c u^r$$

$$A_{\overline{r}} u_{\overline{r}} = A_1 u_1 + A_2 u_2 + \dots + A_n u_n.$$

(c) A comma followed by an additional subscript denotes partial differentiation. A semicolon in place of the comma will indicate that the variable of differentiation is  $x^n$  in place of  $x^k$ .

$$\frac{\partial A::}{\partial x^k} = A::, k$$

$$\frac{\partial A::}{\partial x^k} = A::; k$$

(d) A vertical bar in place of the comma or semicolon will be used for covariant differentiation, the indices being those of a tensor.

2. Our equations (1.1) allow us to perform a good many of the operations possible in Riemannian manifolds, without any hypothesis as to the existence of distance, or of a groundform. The usual formulæ for covariant differentiation holds. We have a parallelism, and thence the equation of "paths," i.e., curves having autoparallel tangents :

$$(2.1) \quad \ddot{x}^i + \Gamma_{jk}^i \dot{x}^j \dot{x}^k = 0$$

$$\dot{x}^i + \Gamma_{jk}^i \dot{x}^j \dot{x}^k = a \dot{x}^i \quad [\text{Schouten}]$$



One operates with the  $\Gamma$ 's precisely as with Christoffel symbols of the second kind in a Riemannian space, and thus obtains a mixed curvature tensor

$$(2.2) \quad R_{ijk}^h = \Gamma_{ik,j}^h - \Gamma_{ij,k}^h + \Gamma_{ik}^m \Gamma_{mj}^h - \Gamma_{ji}^m \Gamma_{mk}^h$$

Even more general results as the theorem of Fermi can be extended. The principal difficulty arises in discussing the problems of mathematical physics. There is no way of defining the magnitude of vectors, no way in which an index can be raised or lowered, i.e., covariant and contravariant tensors associated. Laplace's equation

$$(2.3) \quad \Delta V = \text{div. grad. } V = 0$$

cannot be expressed, as the divergence of a covariant vector cannot be defined here. Similarly, the famous gravitational equations of the older Einsteinian theory

$$R_{ij} - \frac{1}{2} R g_{ij} = \lambda T_{ij}$$

lack a basis of deduction, the  $g_{ij}$  having no meaning. The restricted case

$$R_{ijh}^h = R_{ij} = 0$$

can still be treated, though on a purely formal basis.

Thus, it is not immediately profitable to investigate space-time, and the possibilities of a physical world based on a set of  $\Gamma$ 's that differ but little from their Euclidean or Galilean values, which are all null. A first step must therefore investigate the possibilities of measuring "distance," of founding the affine manifold on a Riemannian. If we assume or define the paths of our geometry to be the actual paths of material particles, or of disturbances in space-time, the geodesics of older speech, an added contact is established with material reality.

We take the path equations (2.1) as our starting point. Symmetry of the  $\Gamma$ 's

$$(2.6) \quad \Gamma_{jk}^i = \Gamma_{kj}^i$$

may be assumed from the algebraic symmetry of (2.1) without loss of generality. To discuss the existence of a Riemannian groundform,

$$(2.7) \quad \left( \frac{ds}{dt} \right)^2 = g_{ij} \dot{x}^i \dot{x}^j$$

is equivalent to discussing the solutions of

$$(2.8) \quad g_i g_{ij|k} = 0$$

$$g_{ij,k} = g_{ih} \Gamma_{jk}^h + g_{hj} \Gamma_{ik}^h$$

The above system of partial differential equation being the familiar system of Koenig, is completely integrable if the compatibility conditions

$$(2.9) \quad g_{ih} R_{jkl}^h + g_{jh} R_{ikl}^h = 0$$

are fulfilled. If identically, we have  $R_{ijk}^h = 0$  and the totally uninteresting case of a flat or Galilean space. If not, further conditions can be derived (Eisenhart).

$$(2.10) \quad g_{ih} R_{jkl/m}^h + g_{jh} R_{ikl/m}^h = 0$$

by covariant differentiation of (2.9). The process must lead to the sets of solutions, or to the absence of any. The method has been brought to a greater degree of elegance by Graustein, for the case of Einstein spaces.

The contracted curvature is the only fundamental covariant tensor of rank two that enters into our theory. If it does not vanish identically, it is natural to build another space using this as a ground-tensor.

$$(2.11) \quad \left( \frac{d\sigma}{dt} \right)^2 = R_{ij} \dot{x}^i \dot{x}^j$$

In this associated space, the operations that we call physical are possible, if  $R = |R_{ij}|$  does not vanish. A co-tensor of rank two can, by the process of finding the normalized co-factors of its square array, be associated with a contravariant tensor of the same rank. The further operations proceed as in any Riemannian space. An Einstein space is one for which the first associate is identically null, or conformal to the original space. One may find a second and further associate spaces, by a continuation of the same process. The difficulty again lies here in the meaninglessness of conformality for affine connections.

I, therefore, propose to approach the problem from another point of view, and to see first the types of metric that can be deduced from a given set of paths. In equations (2.8), the following various properties are expected of the solutions :

(a)  $g_{ij} = g_{ji}$ . If this does not follow from the equations, we can at any rate replace  $g_{ij}$  in the groundform by  $\frac{1}{2} (g_{ij} + g_{ji})$ . It is seen that in general  $g_{ij} + g_{ji} \neq 0$ .

(b)  $g_{ij}$  must be a covariant tensor of rank two.

$$g'_{ij} = g_{mn} \frac{\partial x^m}{\partial x'^i} \frac{\partial x^n}{\partial x'^j} (x \leftarrow x')$$

If the equations are taken as invariant under a point transformation, and we assume

$$g'_{ij} = \phi_{ij}^{mn} g_{mn}$$

a set of relations will be obtained involving  $x$ , the  $y$ 's, the  $\Gamma$ 's, and  $\phi_{\delta}^{\alpha\beta}$  as well as  $x^i, x'^k$ . If it be further demanded that the  $\phi$ 's be purely functions of the transformation,  $(x \leftarrow x')$ , not explicitly dependent on the  $g$ 's or the  $\Gamma$ 's, we have a set of equations satisfied by

$$\phi_{ij}^{mn} = \frac{\partial x^m}{\partial x'^j} \frac{\partial x^n}{\partial x'^i}$$

It does not transpire that these are the only solutions possible, but I do not intend to develop this possible generalization of the tensor here.

(c)  $g = |g_{ij}| \neq 0$ . This is usually another condition added to the equations. If however (2.8) has a solution, it follows that

$$\frac{\partial}{\partial x^k} \log g = \Gamma_{r h}^r$$

The value of  $g$  being other than null initially, it will not vanish.

(d) Continuity, differentiability, and other analytic properties of the  $g$ 's depend on the corresponding properties of the  $\Gamma$ 's. Uniqueness of the solutions does not in general hold, but the various groundforms must give spaces in geodesic correspondence.

(e) The distance  $s$ , represented by

$$\int_{p_0}^p ds,$$

must be stationary over the paths given by (2.1). This is usually written as  $\delta \int \sqrt{g_{ij} \dot{x}^i \dot{x}^j} dt$  with the extra condition  $g_{ij} \dot{x}^i \dot{x}^j = \text{const.}$  along the extremals. We replace it by

$$\delta \int g_{ij} \dot{x}^i \dot{x}^j dt = 0$$

It is intuitively obvious that this will do as well. We can consider the geodesics as the actual trajectories of a particle of unit mass sliding on a smooth hypersurface of the given groundform under a zero potential. The least action formula is precisely the one that we have adopted, and the auxiliary condition is merely the conservation of energy. The Eulerian equations become

$$x \frac{d}{dt} (g_{ij} \dot{x}^j) - g_{k, ij} \dot{x}^k \dot{x}^j = 0.$$

These reduce to  $g_{ij} [\dot{x}^i + \Gamma_{jk}^i \dot{x}^j \dot{x}^k] = 0$  if and only if (2.8) is fulfilled and if  $g$  is not zero, these will be identical with (2.1).

It is the main purpose of this paper to follow the last condition more closely, and to investigate its full significance.

3. Given a single differential equation of the second order

$$(3.1) \quad \ddot{x} + a(x, \dot{x}, t) = 0$$

It is asked whether there exist any functions of  $x, \dot{x}, t$  such that

$$(3.2) \quad \delta \int f(x, \dot{x}, t) dt = 0$$

represents by its extremals the curves that are solutions of (3.1). The Eulerian equation is

$$(3.3) \quad \frac{d}{dt} f_{\dot{x}} - f_x = 0$$

$$\dot{x} f_{x\dot{x}} + \dot{x} f_{\dot{x}\dot{x}} + f_{x\dot{x}} - f_x = 0$$

If then, such an  $f$  exists, the equation (3.3) must be reducible to (3.1) with almost a factor of proportionality,  $\xi(x, \dot{x}, t) \neq 0$

$$\xi [\dot{x} + \alpha] = \frac{d}{dt} f_x - f_x$$

This gives directly,

$$(3.4) \quad \xi = f_{\ddot{x}x}, \quad \xi \alpha = \dot{x} f_{xx} + f_{xt} - f_x, \\ - \alpha f_{\ddot{x}x} + \dot{x} f_{xx} + f_{xt} - f_x = 0$$

And we may state

Theorem 1.—The equation  $\ddot{x} = \alpha(x, \dot{x}, t)$  gives the extremals of  $\delta \int f dt = 0$  if and only if  $f$  is a solution of

$$\alpha \frac{\partial^2 f}{\partial \dot{x}^2} + \dot{x} \frac{\partial^2 f}{\partial \dot{x} \partial x} + \frac{\partial^2 f}{\partial \dot{x} \partial t} - \frac{\partial f}{\partial x} = 0$$

such that

$$\frac{\partial^2 f}{\partial \dot{x}^2} \neq 0$$

Since the partial differential equation always has a solution, we could have stated that every second order differential equation can be deduced from a variational principle. The solution is not unique, as the addition of any perfect differential leaves the Euler equations unchanged. As a corollary, we have,

The linear differential equation

$$\ddot{x} + \dot{x}P(t) + xQ = 0$$

is equivalent to

$$\delta \int e^{\int P dt} \left[ \dot{x}^2 + 2x\dot{x}P - x^2 \left( Q - \frac{dP}{dt} - P^2 \right) \right] dt = 0$$

This could have been derived from inspection after the equation is put in the normal form and the integrand transformed back again. It must be kept in mind that  $cf + \frac{dv(x)}{dt}$  gives the same equation as  $f$ .

The same derivation will now be attempted for systems of second order differential equations.

4. We start with the system

$$(4.1) \quad \ddot{x}^i + \alpha^i(x, \dot{x}, t) = 0 \quad i=1, \dots, n$$

which is to be deduced from

$$(4.2) \quad \delta \int f(x^i, \dot{x}^k, t) dt = 0.$$

Here the single factor of proportionality will be replaced by  $\rho^{ij}(x, \dot{x}, t)$  since both (4.1) and the expanded Euler equations

$$(4.3) \quad \ddot{x}^j f_{\dot{x}^i \dot{x}^j} + \dot{x}^j f_{\dot{x}^i x^j} + f_{\dot{x}^i t} - f_{x^i} = 0$$

are linear in  $\ddot{x}^i$ . This leads to

$$\begin{aligned} \rho_{ij} &= f_{;i;j} \quad \rho_{ij} a^j = \dot{x}^j f_{;i;j} + \frac{\partial}{\partial t} f_{;i} - f_{;i} \\ (4.4) \quad a^i f_{;i;j} - \dot{x}^i f_{;j,i} - \frac{\partial}{\partial t} f_{;j} + f_{;j} &= 0 \quad \left| f_{;i;j} \right| \neq 0. \end{aligned}$$

We may then state the theorem

**Theorem 2.** *The system of equations (4.1) is deducible from a variational principle if and only if there exists a solution of the partial system*

$$a^i \frac{\partial^2 f}{\partial \dot{x}^i \partial \dot{x}^j} - \dot{x}^i \frac{\partial^2 f}{\partial x^i \partial \dot{x}^j} - \frac{\partial^2 f}{\partial \dot{x}^j \partial t} + \frac{\partial f}{\partial x^j} = 0$$

such that

$$\Delta = \left| \frac{\partial^2 f}{\partial \dot{x}^i \partial \dot{x}^j} \right| \neq 0.$$

The solutions of (4.4) exist in general, any perfect differential being one. But I am unable to find directly the necessary and sufficient restrictions on the  $a$ 's for nontriviality represented by  $\Delta \neq 0$ .

It would seem evident, however, that the desired solutions exist much oftener than a groundform exists for affine connections.

Taking the coefficients of affine connection as usual, we investigate the possibility of a special type of metric  $f$ . This  $f$  is to be independent of the parameter  $t$  and expansible as a sum of, or as an uniformly convergent series of polynomials in  $\dot{x}$ , whose coefficients are functions of  $x$  alone.

$$(4.5) \quad f = A + A_i \dot{x}^i + A_{ij} \dot{x}^i \dot{x}^j + \dots + {}^{(n)} A_{i_1 \dots i_k} \dot{x}^{i_1} \dots \dot{x}^{i_k}$$

If  $f$  is to be an invariant, the coefficients must be tensors of rank  $k$ . If we substitute in (4.4) and demand that the result be an identity in  $\dot{x}$ , we get conditions on each set of coefficients

$$(4.6) \quad A_{,k} = 0 \quad A = \text{Const.}$$

$$A_{i,j} \dot{x}^i \equiv A_{j,i} \dot{x}^i \equiv A_{j,i} \dot{x}^i,$$

$$\therefore A_{i,j} = A_{j,i}$$

$$\text{and } A_i \dot{x}^i = \frac{d}{dt} \mu(x).$$

The first two terms are trivial and can be neglected. For the rest

$$\begin{aligned} (4.7) \quad \dot{x}^i \dot{x}^p \dot{x}^m \left[ k(k-1) \left\{ A_{ihp} \Gamma_{lm}^h + A_{ihl} \Gamma_{pm}^h + \dots \right\} \right. \\ \left. - n \left\{ A_{ilm \dots, p} + A_{ilp \dots, m} + \dots \right\} A_{lmp \dots, i} \right] = 0 \end{aligned}$$

Substituting for the ordinary partial derivatives in terms of covariant derivatives, and keeping always in mind the complete symmetry of the  $A$ 's in all their subscripts, we have

$$(4.8) \quad n [A_{ilmr} \dots /_p + A_{ilmp} \dots /_r + \dots - A_{lmrp} \dots /_i] = 0$$

Changing the subscripts in turn with  $i$  and adding, this reduces finally to

$$(4.9) \quad (k) \quad A_{ilmp} \dots /_r = 0$$

Theorem 3.—*A necessary and sufficient condition for the existence of an invariant  $f$  of the type (4.5, is the vanishing of the covariant derivative of the tensor coefficients of rank higher than two. The first two terms, moreover, must be trivial and  $\Delta \neq 0$*

The equations (4.9) again form a system of Koenig, whose conditions of integrability are, on account of the symmetry of the  $A$ 's,

$$R_{ijk}^{h(m)} A_{hi_2i_3} \dots + R_{i,jr}^{h(m)} A_{i,hi_3} \dots + \dots = 0$$

and of course any set that might be derived from these as in (2.10) by further covariant differentiation. In a flat space, these conditions are identically fulfilled, but the most general metric is any  $f$  in which only the  $\dot{x}$  enter. The Galilean metric is the simplest, containing only terms of the lowest degree admissible for non-triviality. Similarly, in the general Riemannian case, we shall in general obtain a wide choice of admissible  $f$  for the given paths; the ground-form is only the non-trivial metric of lowest possible degree.

The parametric case, as also a solution for general  $a^i$  by means of expansion in series is too cumbersome. The next step to be discussed will be a reduction of (4.4) to a system of partial differential equations of the first order.

5. At the end of the second section, under (e), we found the same extremals for two integrands that had the form  $f$  and  $f^2$ . If it be demanded that any function  $\phi(f)$  be a solution of (4.4) with  $f$  itself, we have upon substitution in (4.4)

$$(5.1) \quad \phi'' f_{;j} [a^i f_{;i} - \dot{x}^i f_{;i} - f_t] = 0$$

$\phi''=0$  gives  $\phi = af + b$ .  $f_{;j}=0$  gives  $f=f(x, t)$  both being trivial cases. If (5.1) is to be true for all at least twice differentiable  $\phi$ , it follows that

$$(5.2) \quad a^i \frac{\partial f}{\partial \dot{x}^i} - \dot{x}^i \frac{\partial f}{\partial x^i} - \frac{\partial f}{\partial t} \equiv Df = 0$$

This condition is necessary as well as sufficient, and scrutinised closely, is seen to be precisely  $f=\text{constant}$  along the paths (4.1).

Theorem 4. *A necessary and sufficient condition that the integral of any at least twice differentiable function  $\phi(f)$  be stationary over the extremals of*

$$\delta \int f(x, \dot{x}, t) dt = 0, \quad x \sim x^i, \\ \dot{x} \sim \dot{x}^j$$

is that  $f$  be constant along those extremals. As a rule, the auxiliary condition  $f = \text{constant}$  along the extremals is a restriction on the choice of parameter, and in no case can it modify the form of the Eulerian differential equations.

The equation (5.2) will therefore be adjoined to the system (4.4). Differentiating (5.2) with respect to  $\dot{x}$ , and substituting in (4.4), a first order system results

$$(5.3) \quad \frac{\partial \alpha^i}{\partial \dot{x}^j} \frac{\partial f}{\partial \dot{x}^i} - 2 \frac{\partial f}{\partial x^j} \equiv D_j f = 0.$$

**Theorem 5.** *The existence of solution of (5.2) and (5.3) is necessary and sufficient for the deduction of (4.1) from a variational principle. Then any, at least twice differentiable function of the integrand is also a solution, and the integrand will in all cases be a constant along the extremals.*

A first condition of compatibility is seen by solving (5.3) for  $f_{,j}$  and substituting in (5.2)

$$(5.4) \quad (\alpha^i - \frac{1}{2} \dot{x}^j \alpha^i_{,j}) \frac{\partial f}{\partial \dot{x}^i} - \frac{\partial f}{\partial t} = 0.$$

If this is not identically satisfied, then it must be adjoined to the original system. If the  $\alpha$ 's are homogeneous of degree two in  $\dot{x}$ , the solution of the system, if any, is independent of the parameter  $t$  though this is not a necessary condition. We might sum up several results in

**Theorem 6.** *If the solution is independent of  $t$  and*

$$\alpha^i(\dot{x}, \lambda \dot{x}, t) \equiv \lambda^2 \alpha^i(x, \dot{x}, t)$$

*then (5.2) and (4.4) are consequences of (5.3).*

The existence theorems for first partial systems are quite well known, whereas for (4.4), they have yet to be deduced. The conditions for our system (5.2) and (5.3) are seen to be

$$(5.5) \quad (DD_j - D_j D) f \equiv Q_j^i \frac{\partial f}{\partial x^i} - \frac{\partial \alpha^i}{\partial x} \frac{\partial f}{\partial \dot{x}^i} = 0$$

$$\text{or, eliminating } \frac{\partial f}{\partial \dot{x}^i} \text{ from (5.3), } P_j^i \frac{\partial f}{\partial \dot{x}^i} = 0$$

$$(D_j D_k - D_k D_j) f \equiv R_{jk}^i \frac{\partial f}{\partial \dot{x}^i} = 0$$

where  $f_{,i}$  is eliminated by virtue of (5.3) wherever it occurs and

$$(5.6) \quad -2 P_j^i = \alpha^r \alpha^i_{,r;j} - \dot{x}^r \alpha^i_{,r;j} - \frac{1}{2} \alpha^r_{,j} \alpha^i_{,r} - \frac{\partial \alpha^i}{\partial t} ; j + 2 \alpha^i_{,j}$$

$$4 R_{jk}^i = 4 R_{kj}^i = \alpha^r_{,k} \alpha^i_{,r;j} + 2 \alpha^i_{,k;j} - \alpha^i_{,j} \alpha^i_{,r;k}$$

These new equations, when identically fulfilled, give us complete integrability of the system under discussion. Otherwise, they must also be adjoined to (5.2), (5.3) and (5.4).

The coefficient of (5.6) are connected with each other by means of the relation

$$(5.7) \quad \frac{\partial P_j^i}{\partial \dot{x}^k} - \frac{\partial P_k^i}{\partial \dot{x}^j} = \frac{3}{2} R_{jk}^i$$

And the usual Riemann-Christoffel tensor is given by

$$(5.8) \quad \frac{\partial R_{jk}^i}{\partial \dot{x}^c} = R_{jk;e}^i = R_{e;kj}^i$$

The process of adducing further sets of equations can be further continued. But as we eliminate  $\frac{\partial f}{\partial x^j}$  at each step, and there are left only homogeneous equations in not more than  $n$  of the equations can be independent. Even if  $n$  equations are found to be independent, there can be only the trivial solution  $f=f(x, t)$  inasmuch as  $f; i = 0$

**Theorem 7.** *A necessary condition that there exist a nontrivial solution of the system (5.2) and (5.3) is that the matrix of coefficients of (5.5) and all other derived equations containing only  $f; i$  be of rank less than  $n$ .*

The condition will be seen to be sufficient when  $f$  is to be non-parametric, or when the  $\alpha$ 's are given homogeneous of degree two in  $\dot{x}$ .

If an invariant and non-degenerate  $f$  is found to exist, we have a "space" very similar to the Riemann spaces, and, in fact, the condition of non-triviality suggests a groundform

$$g_{ij} = f_{,i} f_{,j} = f; i; j.$$

This can always be justified, if  $f$  satisfies a relation of the form

$$\dot{x}^i \dot{x}^j f; i; j = \phi(f) + \frac{d}{dt} \psi(x, t),$$

$\phi(f)$  being any at least twice differentiable function of  $f$  itself. The invariance of  $f$  will necessarily make  $f; i; j$  a tensor of rank two, covariant in the indices. Physical problems can then be discussed, and conformality has a meaning. We get the obvious generalizations of Einstein spaces and of the associate spaces as well that need not be discussed here. The equations (5.3) as also (4.4) are generalizations of the vanishing of the covariant derivatives of the fundamental tensor. The coefficients  $R_{jk}^i$  and  $P_j^i$  are actually tensors, if the tensor-invariance of the path equations is known.\*

Developments and geometrical interpretations of the various fundamental conditions in the calculus of variations such as the conditions of Legendre, Jacobi, Weierstrass, the equations of transversality, and the question of conjugate foci,

\* All the differential invariants of the "space" can be had by considering the coefficients of our successive derived equations that contain only  $\frac{\partial t}{\partial \dot{x}}$ .



all of which should be fundamental in our new geometry, will be left to a later paper, or to abler analysts. Parallelism and covariant differentiation are fundamental concepts in recent differential geometry, which have received no consideration here. I shall leave all of these aside, and conclude the paper with a series of remarks, all compressed into one section :

6. (a) The general inverse variational problem can be stated as follows :

GIVEN : A set of differential equations in any number of variables of any given order, partial or ordinary, and a set of auxiliary conditions not a consequence of the differential equations,

TO FIND : Whether or not the manifolds of the solutions of the given equations can be made to coincide for some region with the extremals of a variational problem.

It would seem simpler to discuss the whole problem for ordinary differential equations by means of reduction to a system of ordinary first order differential systems, and then consider the possibility of equating this system to a Plaffian variational principle say, a generalized Hamiltonian principle. This will also give us systems of first order partial differential equations, but unfortunately in several unknowns, for which I have been unable to find any elegant method of solution. When there is to be discussed the problem of fractional differential equations also, no method at all is to be seen. For, the generalized derivative cannot be uniquely defined, as a rule, and may not be real for real variables. The direct problem of the calculus of variations does not seem to have been solved when the generalized derivative enters into the integrand.

(b) A space with trivial metric is not necessarily uninteresting. Take for instance,  $f$  as a perfect differential. The distance of two points is independent of the path, provided  $f$  is non-singular in regions with the proper connectivity, and often, even then. Such a space will have the additive property of distance on a line

$$D(P_1 P_2) + D(P_2 P_3) = D(P_1 P_3)$$

direction has no significance, and the relativist who attempts to locate his neighbours by means of light-signals will be in some difficulty unless he has more than one origin of observation.

(c) Consider the following differential equations that occur so often in mathematical physics :

$$\begin{aligned} \ddot{x} - \lambda \dot{y} - v_x &= 0 \\ \ddot{y} + \lambda \dot{x} - v_y &= 0 \end{aligned} \quad (6.1)$$

They are the simplest example of "non-energetic" forces in a dynamical system. We see them in the restricted problem of three bodies, the vibrations of an infinite cylinder in a circulating fluid, an electron in a magnetic field, the gyroscopic pendulum, and so on, even to the Zeemann effect. By inspection, we deduce these when  $\lambda$  is a constant from

$$\delta \int (\bar{T} + \bar{U}) = 0 \quad (6.2)$$

$$\overline{T} = \frac{1}{2}(\dot{x}^2 + \dot{y}^2) - \frac{\lambda}{4}(\dot{x}y - x\dot{y}) \quad \overline{U} = U - \frac{\lambda}{4}(xy - x\dot{y}).$$

And it is seen that there is still the energy integral in the form  $\overline{T} - \overline{U} = \text{constant}$ . For  $\lambda$  not a constant but a function of position, and parameter, we may apply the methods of the previous paragraph. But as the integrand itself is not constant along the extremals, the general problem comes to that of finding the solutions of two equations of the second order, and not our reducible case. This again calls for a profounder study of the relation between the forms of the integrals and the conditions of compatibility.

(d) The method of the paper is also extensible to partial differential equations, and as an example of the most general procedure for a partial differential equation of the second order, we shall show that the equation of wave mechanics, known as Schrödinger's equation, cannot be deduced from a variational principle.

Compare the equation

$$(6.3) \quad \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2} + \Omega(p, q, r, s, x, y, z, t, u) = 0$$

$$p = \frac{\partial u}{\partial x}; \quad q = \frac{\partial u}{\partial y}; \quad r = \frac{\partial u}{\partial z}; \quad s = \frac{\partial u}{\partial t}$$

to the Euler equation for

$$(6.4) \quad \delta \int_V f(x, y, z, t, p, q, r, s, u) dv = 0.$$

Using again, a factor of proportionality  $\rho(p, q, \dots, u)$  we have the following relationships:

$$(6.5) \quad \begin{aligned} f_{pp} &= f_{zz} = f_{rr} = \rho \\ f_{ss} &= f_{pz} = f_{zr} = f_{rp} = f_{ps} = \dots = 0 \\ \rho \Omega &= p f_{pu} + z f_{zu} + r f_{ru} + s f_{su} + f_{px} + f_{zy} + f_r + f_{st} - f_u \end{aligned}$$

Differentiate the last of these partially with respect to  $p, q, r, s$  and using the others, we have again a system of first partial differential equations, which is:

$$(6.6) \quad \begin{aligned} \sigma &= \log \rho \\ \frac{\partial \sigma}{\partial x} + p \frac{\partial \sigma}{\partial u} - \Omega \frac{\partial \sigma}{\partial p} &= \Omega_p \\ \frac{\partial \sigma}{\partial y} + q \frac{\partial \sigma}{\partial u} - \Omega \frac{\partial \sigma}{\partial q} &= \Omega_q \\ \frac{\partial \sigma}{\partial z} + r \frac{\partial \sigma}{\partial u} - \Omega \frac{\partial \sigma}{\partial r} &= \Omega_r \\ \frac{\partial \sigma}{\partial t} &= - \frac{\Omega_s}{\Omega} \end{aligned}$$

In the equation of Schrödinger,  $\Omega$  has the form  $\lambda s + u \nabla(xy)$ . The following are the derived equations, easily seen to be incompatible with above :

$$(a): (6.7) \quad (\Omega_y + q \Omega_u) \frac{\partial \sigma}{\partial p} - (\Omega_x + p \Omega_u) \frac{\partial \sigma}{\partial q} = 0$$

and two others by cyclic rotation of letters.

$$(b): \quad \frac{\partial \sigma}{\partial p} = \Omega^2 (\Omega_x + p \Omega_u)$$

and two others by cyclic rotation of the letters.

These are consistent among themselves, but further derived sets give the contradiction.

Theorem 8. *Schrödinger's wave equation in its general form is not derivable from a variational principle.*

It is well to note here that the  $u$  in the wave equation is taken to be complex as also that the classic derivation by Pauli and Heisenberg is based on the physical assumption of Eigenwerte.

(e) The analogy between the derivation of ordinary equations from a minimum principle and that of differential equations from a variational principle is easily worked out.

Given the equations

$$(6.8) \quad f^i(x^1, x^2, \dots, x^n) = 0 \quad i=1 \dots n,$$

It is desired to equate the whole set to a single minimum principle

$$dF(x^1, x^2, \dots, x^n) = 0.$$

Using again our integrating factors  $\rho_{ij}(x^1 \dots x^n)$

$$\rho_{ij} f^j = \frac{\partial F}{\partial x^i}.$$

That gives the following partial differential equations for the  $\rho$ 's :

$$(6.9) \quad (\rho_{ij} f^j)_{,k} - (\rho_{kj} f^j)_{,i} = 0$$

A simple solution is

$$\rho_{ij} = \frac{\partial f^j}{\partial x^i}.$$

Theorem 9. The equations  $f^i(x^1, x^2, \dots, x^n) = 0$  can be derived from  $dF = 0$ , if the Jacobian  $\left| \frac{\partial f^i}{\partial x^j} \right|$  does not vanish. One such  $F$  is  $\sum_{i=1}^n (f^i)^2$ .

#### References.

<sup>1</sup> E. P. Eisenhart, *Riemannian Geometry*.

<sup>2</sup> E. P. Eisenhart, *Non-Riemannian Geometry*.

<sup>3</sup> T. Levi-Civita, *The Absolute Differential Calculus*.

<sup>4</sup> G. D. Birkhoff, *Dynamical Systems*.

<sup>5</sup> M. Janet, *Leçons sur les Systèmes d'équations aux dérivées partielles*.

<sup>6</sup> J. A. Schouten, *Der Ricci-Kalkül*.

# THE PHENOMENON OF 'AFTER EFFECT' AND 'INDUCTION PERIOD' IN THE REVERSIBLE PHOTOCHEMICAL REDUCTION OF TUNGSTIC ACID SOL.

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Received on 19th March, 1932.

In a previous paper<sup>1</sup> we have shown that the photochemical reduction of the sols of molybdic and tungstic acids by ethyl alcohol follows the zero molecular law in presence of sunlight. Reduction cannot be observed in the dark.

We tried to study the photochemical reduction of these sols in the ultra-violet light received from a mercury lamp. The sols are reduced and the blue colour is seen, but the rate of reaction is very slow, and hence no quantitative work could be done.

In this paper we shall present the result obtained on the period of induction and after effect in the photochemical reduction of tungstic acid by glucose in presence of sunlight.

The appearance of blue colour was followed by a Nutting's spectro-photometer. To isolate any particular region of the spectrum for the case of comparison, a shuttered eye-piece was employed. To obtain extinction coefficient, the Bunsen-Roscoe formula was employed and readings were taken on the 'Density Scale' of the rotating circle. Thus the extinction coefficient is given  $\Sigma = \frac{D}{t}$  where D is the reading on the density scale and equal to  $2 \log_{10} \tan \theta$ ,  $\theta$  being the angular reading and  $t$  the thickness in centimeters of the absorbing substance.

The following are the experimental results on the 'period of induction.'

Table 1

5c.c. 3 per cent sodium tungstate + 1c.c. N/1.06 HCl + 10 c.c. glucose + 10c.c. HO<sub>2</sub>.

| Time in mins. | Extinction Coefficient | K <sub>0</sub> Zero molecular |
|---------------|------------------------|-------------------------------|
| 0             | 0                      | ...                           |
| 1             | 0                      | ...                           |
| 2             | 0                      | ...                           |
| 3             | 0.02                   | 0.0067                        |
| 4             | 0.02                   | 0.0050                        |
| 5             | 0.03                   | 0.0060                        |
| 8             | 0.06                   | 0.0075                        |

| Time in mins.                 | Extinction Coefficient | $K_0$ Zero molecular |
|-------------------------------|------------------------|----------------------|
| 12 Taking as initial reading. | 0.08                   | 0.010                |
| 14                            | 0.10                   | 0.010                |
| 16                            | 0.12                   | 0.010                |
| 18                            | 0.14                   | 0.010                |
| 20                            | 0.16                   | 0.010                |
| 22                            | 0.18                   | 0.010                |
| 24                            | 0.20                   | 0.010                |

From the above table it is clear that there is a period of induction in this photochemical reduction. It takes 3 minutes to start the reaction and then it gradually increases up to 8 minutes after which if we calculate the rate of reaction we find that it obeys zero molecular law. This period of induction is probably due to the fact that there are aggregated molecules present in tungstic acid which are not active as simple molecules. Hence it appears that by the action of light at first the aggregated molecules break up into simple molecules and then the reduction begins.

With a view to study the after effect phenomenon, the solution was exposed to light for some time and then it was kept in the dark and the readings were taken. The following are the experimental results :—

Table 2

Concentration of solution as given in table 1. Exposed to sunlight for 20 minutes.

| Time in mins. | Extinction Coefficient | $K_0$ Zero molecular |
|---------------|------------------------|----------------------|
| 20            | 0.16                   |                      |
| 24            | 0.12                   | 0.010                |
| 28            | 0.07                   | 0.011                |
| 30            | 0.04                   | 0.012                |
| 32            | 0                      | 0.013                |

The above results show that the reduced tungstic acid, which yields a coloured solution is oxidised to colourless tungstic acid when kept in the dark and the photochemical reduction of tungstic acid sol appears to be reversible. The constants calculated for the oxidation of the reduced tungstic acid is found to be increasing. The reversible reaction, *viz.*, the oxidation is at the beginning a little balanced by the direct action due to after effect.

#### INFLUENCE OF CARBON DIOXIDE IN THE REACTION

In order to study whether the oxidation of the reduced tungstic acid is due to the reverse reaction or to the action of air we carried out the experiments in an atmosphere of carbon dioxide. The following are the results ;

Table 3

Exposed to sunlight. Concentration of the solution as in table 1.

| Time in mins. | Extinction Coefficient | K <sub>0</sub> Zero molecular |
|---------------|------------------------|-------------------------------|
| 0             | ...                    | ...                           |
| 3             | 0.25                   | ...                           |
| 12            | 0.40                   | 0.017                         |
| 21            | 0.55                   | 0.017                         |
| 30            | 0.72                   | 0.0174                        |
| 39            | 0.86                   | 0.0170                        |
| 48            | 0.95                   | 0.0156                        |
| 51            | 0.97                   | 0.0150                        |
| 60            | 1.02                   | 0.0135                        |
| 65            | 1.02                   | ...                           |
| 70            | 1.02                   | ...                           |

From the above table we see that the rate of reduction is much greater than that observed in table 1. The reduction is complete in one hour, after that there is no increase in the extinction coefficient.

In order to find the 'after effect' we exposed the solution in sunlight for some time and then kept it in the dark. The experiment is carried out in an atmosphere of carbon dioxide in order to stop the oxidation of the reduced acid by air. The results are given below.

Table 4

Exposed for 16 minutes and then brought in the dark.

| Time in mins. | Extinction Coefficient | K <sub>0</sub> Zero molecular |
|---------------|------------------------|-------------------------------|
| 16            | 0.48                   | ...                           |
| 19            | 0.51                   | 0.010                         |
| 22            | 0.53                   | 0.008                         |
| 25            | 0.53                   | ...                           |
| 30            | 0.53                   | ...                           |

Exposed for 39 minutes and then brought in the dark.

| Time in mins. | Extinction Coefficient | K <sub>0</sub> Zero molecular |
|---------------|------------------------|-------------------------------|
| 39            | 0.85                   | ...                           |
| 42            | 0.88                   | 0.010                         |
| 45            | 0.90                   | 0.008                         |
| 48            | 0.91                   | 0.0067                        |
| 51            | 0.91                   | ...                           |
| 55            | 0.91                   | ...                           |

The foregoing results conclusively prove that there is influence of after effect for some time and then a stationary state is reached when the reaction is studied in absence of air. This further shows that by passing carbon dioxide no oxidation of the reduced acid is observed and we are of opinion that the apparent reversibility of the reaction is due to the oxidising action of air.

The phenomenon of after effect has been shown to be present in several photochemical reactions by Mukherji and Dhar.<sup>2</sup> We are of opinion that the after effect is due to the increase in the life period of the activated molecules in solution.

We desire to express our best thanks to Prof. N. R. Dhar for his kind interest and encouragement in the progress of this work.

*References:*

<sup>1</sup> Ghosh and Bhattacharya, *Ind. Chem. Soc. J. urn.* 7., 711., 1930.

<sup>2</sup> Mukherji and Dhar, *Ind. Chem. Soc. Journ.* 2, 227, 1926 ; 5, 204, 1928.

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# THE ABSORPTION SPECTRA OF LITHIUM HALIDES AND THE LATENT HEAT OF EVAPORATION OF LITHIUM.

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The latent heat of evaporation of a metal is usually determined from its vapour pressure data, according to the equation,

$$L_M = \frac{R T_1 T_2}{T_1 - T_2} \log_e \frac{P_1}{P_2} \quad \dots \quad \dots \quad \dots \quad (1)$$

where R is a constant = 1.985, and  $P_1$  and  $P_2$  are the vapour pressures of the metal M at the absolute temperatures  $T_1$  and  $T_2$  which are close to each other. The vapour pressure of lithium is yet unknown, hence the latent heat of evaporation has not yet been determined.

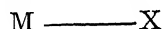
In the present paper I have determined the latent heat of evaporation of lithium by studying the absorption spectra of the vapours of the halides of lithium experimentally and interpreting the results of the experiments in the light of Franck's<sup>1</sup> theory of photo-dissociation of alkali-halides. A short theory of the experiment is given below.

## THEORY

In the normal molecule of a diatomic halide the two parts of the molecule have opposite charges and they are bound together by a large electrostatic force of attraction as,



When such a molecule is exposed to the energy from a source of continuous light, light of suitable frequency is absorbed and the molecule is raised to higher electronic state, the result is that the electron passes from the halogen to the metal and the electrostatic force is destroyed. Now the combination,



being unstable, dissociation takes place and the molecule is split up into two normal atoms. At this stage of atomic dissociation, the two atoms can separate with any amount of kinetic energy; hence light is absorbed continuously from the source and the absorption begins from a long wavelength limit  $\lambda$ , and gradually extends towards the shorter wavelength side. We have the relation

$$R = Q + \frac{1}{2} D_{x_2} + L_M - L$$

$$\text{or } L_M = R + L - [Q + \frac{1}{2} D_{x_2}] \quad \dots \quad \dots \quad \dots \quad (2)$$



$$\text{where } R = N \frac{h\nu}{J} \quad \dots \quad (3)$$

$$= \frac{286000}{\lambda}$$

where  $\lambda$  is the long wavelength limit of absorption in Å. units,  $D$  = the heat of dissociation of the halogen,  $L_M$  and  $L$  are the latent heats of the metal and the halide respectively, and  $Q$  = heat of formation of the compound in the solid state.

$R$  is obtained from the results of the absorption experiments, and the other quantities are taken from Landolt and Börnstein's Tables.<sup>2</sup> Thus, the only unknown quantity  $L_M$  can be calculated.

#### THE EXPERIMENT.

In order to study the absorption spectra, I took anhydrous lithium halides and vaporised them in the Vacuum Graphite Furnace<sup>3</sup> of this laboratory in an atmosphere of nitrogen. Continuous light was passed through the vapours and their absorption spectra photographed.

The source of continuous light was a specially constructed hydrogen discharge tube run by a high current transformer. The spectrum was photographed with Hilger E3 quartz spectrograph, and micro-photograms were taken on the Carl Ziess Microphotometer at Patna laboratory. The curves obtained are given in Fig. II.

#### THE RESULTS OF THE EXPERIMENT.

The photographs show continuous absorption beginning from an ill-defined long wavelength limit and gradually extends towards the shorter wavelength side. In the case of the bromide and the iodide there are re-transmissions and again absorption. The first absorption limits and the corresponding values of  $R$  are tabulated in Table I below:—

Table I

| Halide | Beginning of absorption<br>in Å. U. | R in k.cals. |
|--------|-------------------------------------|--------------|
| LiF    | 2160                                | 132.4        |
| LiCl   | 2420                                | 118.0        |
| LiBr   | 2735                                | 104.5        |
| LiI    | 3640                                | 78.5         |

The other data (taken directly from Landolt and Börnstein's Tables) is collected in Table II given below :—

Table II

| Halide | Q    | $\frac{1}{2} D_{\infty_2}$ | $L_M$ |
|--------|------|----------------------------|-------|
| LiF    | 120  | 38*                        | 55    |
| LiCl   | 97   | 29                         | 37    |
| LiBr   | 87   | 23                         | 35.7  |
| LiI    | 71.3 | 17.3                       | 40    |

## CALCULATIONS

We have the equation (2) in the case of lithium halide as

$$L_{Li} = R - Q - \frac{1}{2} D_{\infty_2} + L$$

Substituting the values for the quantities on the right-hand side of the equation we have,

In the case of LiF,

$$\begin{aligned} L_{Li} &= 132.4 - 120 - 38 + 55 \\ &= 29.4 \text{ k.cals.} \end{aligned}$$

In the case of LiCl,

$$\begin{aligned} L_{Li} &= 118 - 97 - 29 + 37 \\ &= 29.0 \text{ k.cals.} \end{aligned}$$

In the case of LiBr,

$$\begin{aligned} L_{Li} &= 104.5 - 87 - 23 + 35.7 \\ &= 30.2 \text{ k.cals.} \end{aligned}$$

In the case of LiI,

$$\begin{aligned} L_{Li} &= 78.5 - 71.3 - 17.3 + 40 \\ &= 29.9 \text{ k.cals.} \end{aligned}$$

Thus the values of  $L_{Li}$  are : —

Table III

| Halide | $L_{Li}$ |
|--------|----------|
| LiF    | 29.4     |
| LiCl   | 29.0     |
| LiBr   | 30.2     |
| LiI    | 29.9     |

\*  $D_{F_2} = 76$ , k.cal. This value has been determined by the author and reported in the *Proc. Roy. Soc.* 136 (1932), p. 76,

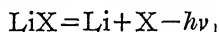
Therefore the mean value of

$$L_{Li} = (29.6 \pm .6) \text{ k.cals.}$$

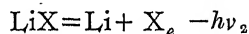
*Re-transmission.*

In the cases of the absorption due to the bromide and the iodide of lithium, we obtain retransmission.

The first absorption corresponds to the dissociation,



while the second absorption is due to the splitting up of the molecule into one normal and another excited atom. Assuming that the halogen is excited, we have,



If  $\Delta\nu$  is the difference of frequency corresponding to the two absorptions  $h(\nu_2 - \nu_1)$ , we have E the energy of excitation,

$$E = \frac{\Delta\nu}{8100} \text{ volts} \quad \dots \quad \dots \quad \dots \quad (4)$$

The actual values observed as the result of these experiments are:—

$$\begin{array}{llllll} LiBr & \dots & \dots & \Delta\nu = 3770 & \dots & E = 0.46 \text{ volts} \\ LiI & \dots & \dots & \Delta\nu = 7300 & \dots & E = 0.91 \text{ volts} \end{array}$$

The frequency differences obtained by other spectroscopic methods are:

$$\begin{array}{llllll} \text{For Br...} & \dots & \Delta\nu = 3633 & \dots & E = 0.448 \text{ volts} \\ \text{For I ...} & \dots & \Delta\nu = 7600 & \dots & E = 0.938 \text{ volts} \end{array}$$

Figs. I<sub>b</sub> and I<sub>c</sub> show the retransmissions and II<sub>c</sub> and II<sub>d</sub> and show the microphotograms for the retransmission plates.

### THE DISCUSSION OF THE RESULTS.

According to the present determination, the latent heat of evaporation of Lithium is 29.6 k. cal. Unfortunately no work has yet been done on the accurate determination of the vapour pressure of Lithium, hence it is not possible to check the above value. But some rough calculation can be given in support of the value obtained.

The vapour pressure of sodium has been investigated in great detail by Ladenburg and Thiele.\* They expressed the observed vapour pressure by the empirical formula,

$$\log p = -\frac{26077}{4.573 \times T} - 1.178 \log T + 11.329 \quad \dots \quad (5)$$

where  $p$  is the vapour pressure in mms. of mercury and  $T$  is the absolute temperature, and the number 26077 stands for  $L_{Na}$  (in cal.).

Now the constant in the formula contains the term  $\frac{3}{2} \log M$ , as the "chemical constant" and is given by

$$C = -1.588 + \frac{3}{2} \log M \quad \dots \quad \dots \quad (6)$$

where  $M$  is the atomic weight of the element.

The chemical constant of lithium should be less than that of sodium, by  $\frac{3}{2} \log \frac{23}{7}$ , i.e., by 0.775. Further as lithium and sodium are very much alike in chemical and physical properties, we suppose that their atomic specific heat terms are almost equal, and their dissociation into atoms is also alike. We thus obtain in the case of Lithium:

$$\log P_{\text{Li}} = -\frac{L_{\text{Li}}}{4.573 \times T} - 1.178 \log T + 10.554 \quad \dots \quad (7)$$

By taking the conditions corresponding to the boiling point of Lithium, the value of  $L_{\text{Li}}$  can be approximately calculated. According to Landolt and Börnstein's Tables the boiling point of Lithium is  $T^\circ = 1400^\circ \text{C}$  or  $1673^\circ \text{Abs.}$  Putting  $T = 1673$  and corresponding  $p = 760$  mms. in the formula (7), we have,

$$\log 760 = -\frac{L_{\text{Li}}}{4.573 \times 1673} - 1.178 \log 1673 + 10.554 \quad \dots \quad (8)$$

which gives

$$\begin{aligned} L_{\text{Li}} &= 29570 \text{ cal.} \\ &= 29.57 \text{ k.cals.} \end{aligned}$$

Thus it can be seen that the value of  $L_{\text{Li}} = 29.6$  k. cal. found out by this new method is in excellent agreement with that expected from the theory. Though the method applied to check the present result is rough still it can be said that the value is not much far from the real one.

As regards the excitation potentials of bromine and iodine, the results obtained by the experiments are quite near the actual values. Taking into consideration the difficulty in reading the exact beginning of absorption, from the plate we see that the results obtained are quite true within experimental errors.

*(Note added during proof correction)*

After this paper was sent for publication the author has come across a paper by A. Borgos<sup>5</sup> in which the quantity is calculated from the determinations of the vapour pressures of lithium. He gets 28.2 k.cals. The two methods—quite independent of one another—show excellent agreement in the result.

#### SUMMARY.

In the present paper the absorption spectra of the halides of lithium in the vapour state have been obtained. The absorption is continuous beginning gradually from an ill-defined long wavelength limit as in the case of other alkali halides. Using the relation,

$$h\nu = R = Q + \frac{1}{2}D_{\infty_2} + L_{\text{Li}} - L$$

where  $R$  = "atomic heat of dissociation" obtained from the long wavelength limit of absorption, we obtain  $L_{\text{Li}}$  since the other quantities are known.

$L_{Li}$  comes out to be

$$(29.6 \pm .6) \text{ k. cal. per gm. atom}$$

In the case of LiBr, and LiI retransmissions and second absorptions were obtained. Assuming that the second absorption corresponds to the splitting up of the molecule into a normal metal and an excited halogen atom the energy of excitation of the atom is calculated from the frequency difference between the two absorption limits on the long wavelength side. The excitation potentials thus obtained are:—

|    |     |     |     |           |
|----|-----|-----|-----|-----------|
| Br | ... | ... | ... | 0.46 volt |
| I  | ... | ... | ... | 0.91 volt |

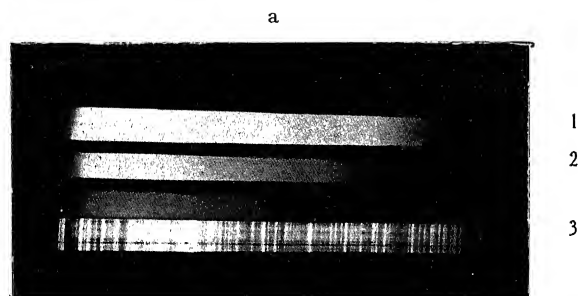
#### ACKNOWLEDGMENTS

My sincere thanks are due to Prof. M. N. Saha, F.R.S., for his kind and invaluable guidance throughout the work.

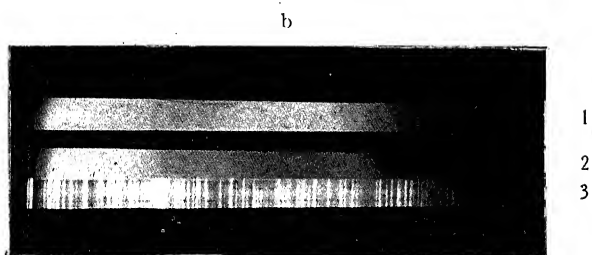
My thanks are also due to Dr. Caldwell, the Principal, and Prof. A. T. Mukerji, the head of the Physics Department, Science College, Patna, for giving me kind permission and facilities to work on the micro-photometer of the Science College, and to Dr. G. B. Banerji for helping me in the actual working with the apparatus.

#### References.

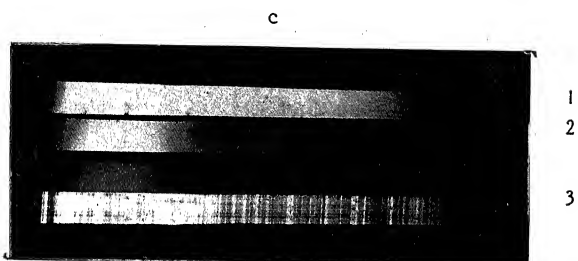
- <sup>1</sup> 'Z. Physik,' Vol. 31, p. 441 (1925).
- <sup>2</sup> Landolt and Börnstein 'Physikalisch Chemische, Tabellen,' 3rd ed. Berlin (1923).
- <sup>3</sup> Vide 'Proc. Roy. Soc. A.' Vol. 136, p. 78 (1932).
- <sup>4</sup> 'Z. Phys. Chem.,' Vol. 7, p. 167 (1930).
- <sup>5</sup> 'Anns. de Phy.' Vol. 17, p. 201, (Mars 1932).



LiCl  
(absorption begins at  $\lambda$  2420)



LiBr  
(absorption begins at  $\lambda$  2735)  
 $\Delta\nu = 3770$



LiI  
(absorption begins at  $\lambda$  3640)  
 $\Delta\nu = 7300$

1—continuous  
2—absorption  
3—Cu-arc

Fig. I

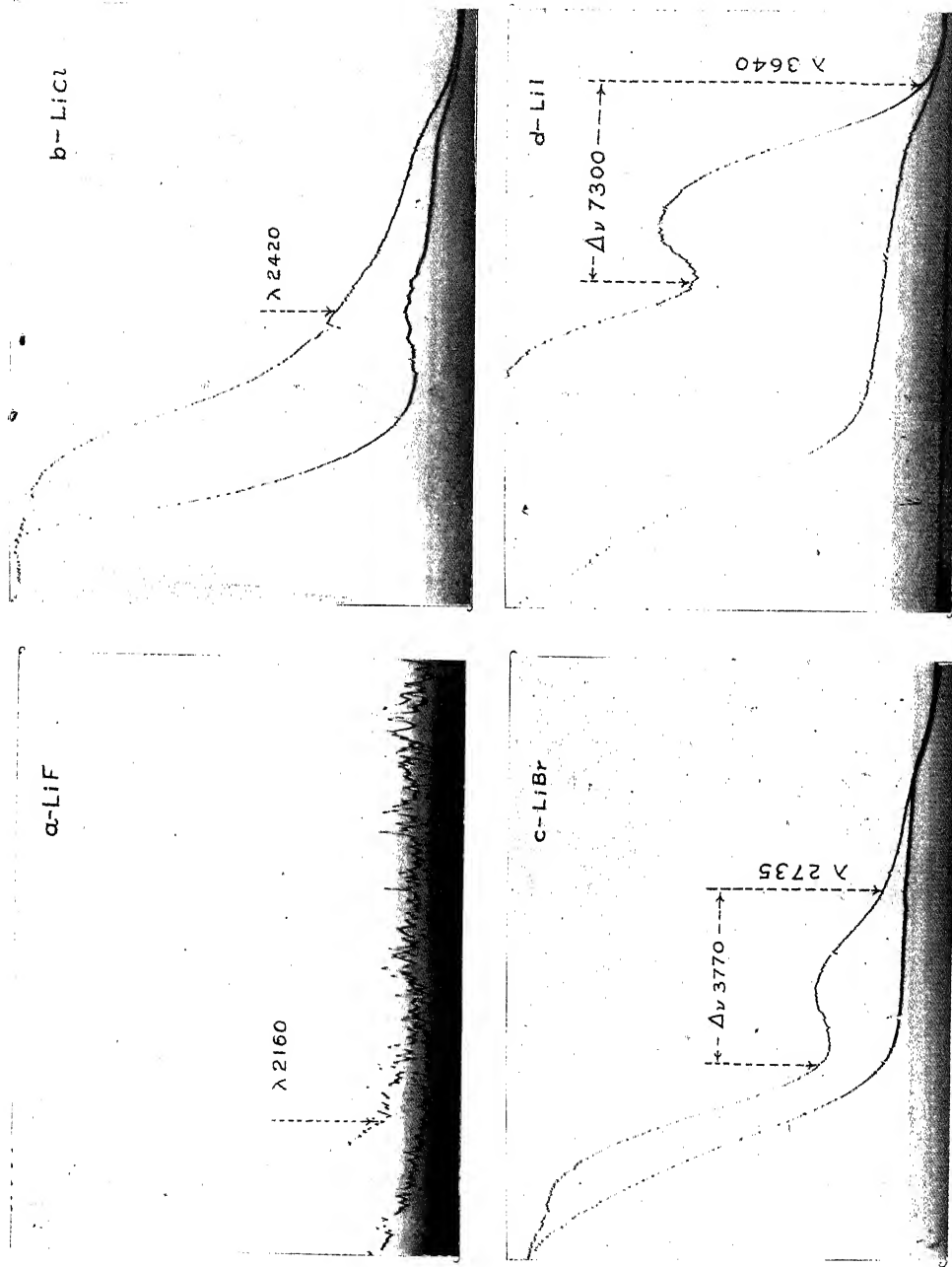


Fig. II

(The Microphotometer used was Carl Zeiss make)

# THE EFFECT OF THE VELOCITY OF HAMMER UPON THE QUALITY OF A NOTE FROM THE STRUCK STRING

## PART I

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## INTRODUCTION

The problems connected with the vibrations of strings with a special reference to piano and the art of piano-playing are of much interest to a physicist as well as to an artist and afford an extensive field for investigation. The particular point whether it is possible to vary the quality of a note along with the loudness, *i.e.*, with the hammer-velocity or independently of it has been much studied and discussed. It has been stated that the quality of a note, apart from its loudness, depends on the relative intensity of the fundamental tone and its several harmonics and that the differences in the quality are noticeable according as whether the same note is struck with a sharp blow or a heavy pressure, and we are led to the conclusion that the intensities of the fundamental tone and its several harmonics are either functions of one variable only or of two or more variables. Now those adhering to the single variable hypothesis assert that the quality of a note may vary according to its loudness; this only requiring that the intensities of the various components shall be different functions of the same variable instead of being its multiples. We are also told that the harmonics of a note are always most prominent when the note has been produced by the least possible hit by the fingers, in fact, when it is practically produced by pressure alone.

Recently Mr. William Braid White<sup>2</sup> made certain observations concerning the variations of quality of a piano-note with its loudness. In his paper three pictures of the sound emitted from the same key, with three different artistic touches, of a concert grand piano are given, in which every curve has its own individual shape corresponding to its individual loudness. These pictures were obtained with the aid of a microphone in conjunction with an amplifier, thus rendering the sound pass through a net-work of electrical system, before it was actually recorded. By a study of these curves he concludes that "every difference of hammer-velocity connotes a difference both of intensity and of tone-color and that it is not possible for a pianist to obtain from the same note two sounds of different color-values (component structures) without a corresponding change of loudness."



In this present paper also a study of the same point has been made by means of a different but direct experimental method and, as will be seen, the results obtained are not in agreement with the conclusions of Mr. W. B. White. In these experiments the loudness of a note was varied by varying the hammer-velocity and the resulting time-displacement curve of one fixed point of the string was studied. It was found that the character of the curve hardly alters although the loudness changes by about 25% or more. Details of the experimental work and discussions are given below.

### EXPERIMENT

The apparatus used in the present investigation was very simple. A piano was not used but instead a steel wire was stretched between two bridges, 140 cms. apart (of which one was a flat bridge and the other a sharp-edged one) along a wooden board, 150 cms. long, 12 cms. broad and 3 cms. thick. Since the temperature variation of the room did not exceed one or two degrees, the tension of the stretched string was assumed to be almost constant. The hammer used was not covered with felt but with a rubber tubing and mechanically it was so arranged that it could strike the wire with widely different velocities by simply allowing it to fall freely from different heights. The actual vibrations set up in the wire were shadow-graphed as is usually done by means of a falling-plate arrangement. A few shadowgraphs of the vibrations of the string obtained by this method, when the hammer, the striking point and the other factors connected with the string were kept constant and only the hammer-velocity was changed, are shown here.

In Fig. (A) curves (1), (2), (3) and (4) are the vibration curves of the string with a particular hammer of mass about 14.6 grams and the striking point at a distance of about 37.5 cms. from the flat bridge. The actual hammer-velocity of impact was not measured, but the hammer was allowed to fall freely upon the string from different heights ranging from about 2.5 cms. to about 6.5 cms. Since no external forces other than the frictional and the gravitational acted upon the hammer before it impinged upon the string—the hammer being in effect an inverted compound pendulum—it is quite obvious that the hammer velocities in these cases differed fairly widely from each other and thus the object of the experiment, *i.e.* varying the hammer-velocity without much changing the mode of this variation was quite fulfilled.

In Fig. (B) curves (1), (2), (3), and (4) are the vibration curves of the same string with a hammer of effective mass about 12.6 grams and the striking point at a distance of 30 cms. from the nearest bridge. In this case also the heights from which the hammer was allowed to fall freely ranged from 2.5 cms. to 6.5 cms.

A very slight difference in the curves Fig. (A) (1), (2), (3) and (4) and also in the curves Fig. (B) (1), (2), (3) and (4) which may be noticed on careful examination is due to the fact that in taking the shadowgraphs, the velocity of the running

photographic plate on which these vibration-curves were recorded was not exactly the same in all the cases. It differed a little in every case so that the elongations of these curves, but not their character, are a bit different from each other. These differences in the elongation, however, have nothing to do with the variations in the hammer-velocity but are mainly due to the non-similarity in the velocity of the recording photographic plate. This point has been confirmed experimentally by keeping the hammer-velocity constant and taking different shadowgraphs with alling-plate velocities differing a little from each other. All such curves (not produced here) indicated the same type of difference due to difference in elongations although the hammer-velocity was not changed. But even then the changes, if any, in the character of the curves Fig. (A) as well as Fig. (B) are not so marked as we find in the curves given by W. B. White.

In curves Fig. (C) (1), (2), (3) and (4) this effect, due to the velocity of the photographic plate not remaining the same was reduced to a minimum; care being taken to keep the velocity of the running photographic plate the same in all the four cases. The effective mass of the hammer used was about 11.9 grams. The distance of the striking point from the flat bridge was 18 cms. The heights from which the hammer fell freely ranged from 2.8 cms. to 7.4 cms. We can see at once that all these curves have the same shape or character although their amplitudes are different from each other.

Thus all the shadowgraphs so far obtained by us have confirmed beyond doubt that if the hammer, the striking point and the other factors of the string remain the same, as is the case with a piano, the resulting vibration of the string or, if preferred, the quality of the sound emitted should remain the same, no matter whatever variations in the hammer-velocity may take place. In fact, a study of all the curves obtained under several different conditions clearly shows that the variation in the hammer-velocity alters only the amplitude of the sound emitted and not its quality. That is to say, for any individual quality of a note there may correspond any number of different amplitudes. Hence we find that the quality of a note is quite independent of its amplitude.

Now in order to test whether the flexural vibrations of the stem of the hammer have any effect upon the quality of the note, we used a special hammer, the stem of which was made out of a piece of thick brass wire so that these effects may be magnified. The effective mass of this hammer was about 9.5 grams and the striking distance was 17.5 grams from the nearest bridge. Two cases of the different modes of giving rise to two different types of flexural vibrations in the stem of the hammer are shown in Fig. (D) curves (1) and (2). It is clearly seen that these curves differ from each other in character as well as in amplitude. It may also be noted that the curve with the larger amplitude appears to be simpler in structure than the other one with the smaller amplitude.

The discussion of the results obtained along with a note on the energy imparted to the struck string and its distribution amongst the partials will be given in Part II of this paper.

In conclusion I thank Dr. R. N. Ghosh, D.Sc. for his guidance and help throughout the work. I also wish to express my thanks to the authorities of the Osmania University, particularly to Principal Mohammed Abdur Rahaman Khan for granting me a scholarship which enabled me to stay at Allahabad and carry out this work.

*References.*

<sup>1</sup> G. H. Bryan, *Nature*, 91, 246, 1913.

<sup>2</sup> W. B. White, *Amer. Acoustic Soc. Journ.* 1, 357, 1930

Fig. (A) (1)

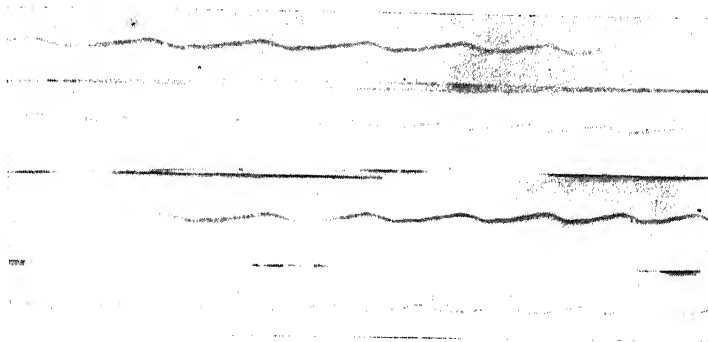


Fig. (B) (1)

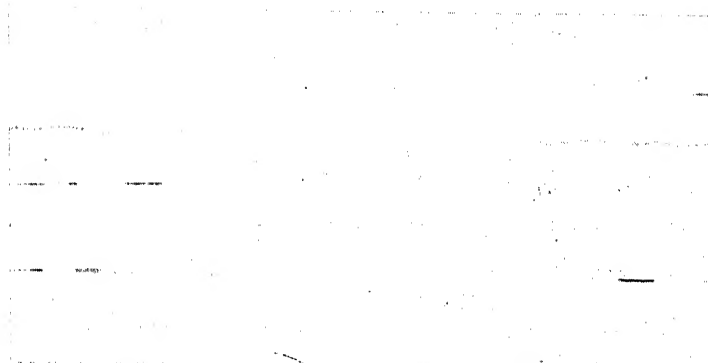


Fig. (C) (1)

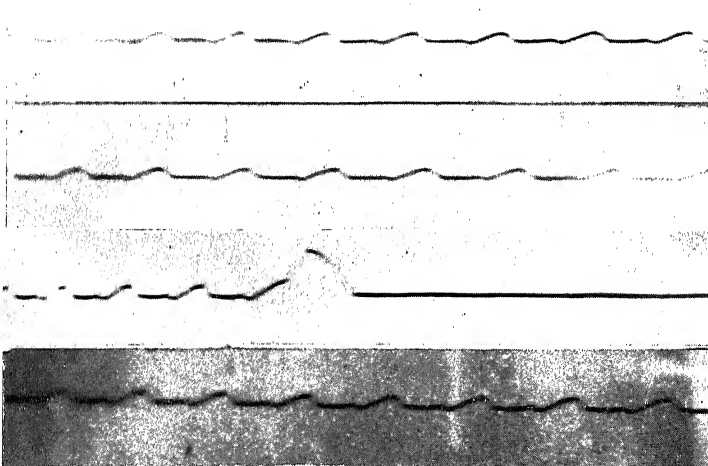
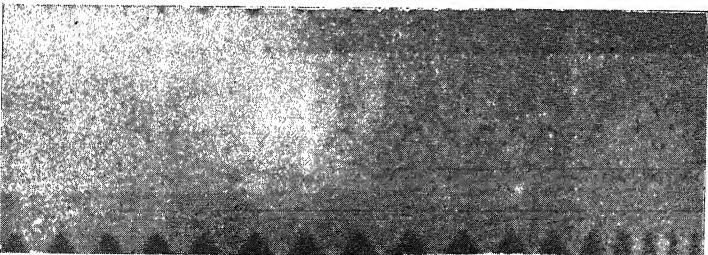


Fig. (D) (1)



# ON THE CLASSIFICATION OF THE SPECTRAL LINES OF $\text{Cl}_V$ AND $\text{Cl}_{IV}$

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## 1. INTRODUCTION

Chlorine is one of those elements the spectrum of which has been studied widely in the Schumann and Lyman regions for the normal and ionised states. The chief workers in the field are Millikan and Bowen,<sup>1</sup> who while studying the nature and position of  $pp'$ -group, excited the spectrum up to the 7th degree of ionisation. The other principal workers in the field are Turner,<sup>2</sup> who photographed the principal lines of the arc spectrum in the Schumann region, Bloch and Bloch,<sup>3</sup> Asagoe,<sup>4</sup> Kiess and de Bruin,<sup>5</sup> and Majumdar.<sup>6</sup> Most of these workers confined themselves to the lower ionised states of the atom. At the present time the classification of the lines up to the second state of ionisation is known.

The object of the present work is the classification of the lines of chlorine in the fourth and fifth stages of ionisation. I have taken, as my starting point, Bowen's work<sup>7</sup> in the Schumann region on the series spectra of  $\text{Cl}_{II}$ ,  $\text{Cl}_{III}$ ,  $\text{Cl}_{IV}$  and  $\text{Cl}_V$ . For  $\text{Cl}_V$  he gave a number of lines in the region between  $\lambda$  390'07, and 894'15 and put forward a scheme of classification along with it; later he published a classification of a number of lines for  $\text{Cl}_{IV}$  in region between  $\lambda$  463'011 to 985'749. But the nature of the spectra of these ions in the visible and ultraviolet is totally unknown, though lines due to them have been given by the Blochs, Asagoe and others.

## II. Theoretical consideration in the spectra of 3-valence electron systems

The electron structure in this system is as follows :

Table 1.

| Electron structure | Term  | Electron structure | term                 |
|--------------------|-------|--------------------|----------------------|
| $ns^2np$           | $^2P$ |                    |                      |
| $ns^2nd$           | $^2D$ |                    |                      |
| $ns^2(n+1)s$       | $^2S$ | $ns.np^2$          | $^4P, ^2D, ^2P, ^2S$ |
| $ns^2(n+1)p$       | $^2P$ | $np^3$             | $^2D, ^2P, ^2S$      |

( $n$  has the value 3 in the case of  $Cl_V$ )

The first four rows on the left give the terms from the normal configuration  $ns^2$  of the next higher ion, the first row on the right hand gives the terms from  $ns np$ -configuration of the ion, and in the second row, those terms which arise from  $np^3$  are recorded.

## III. Position of the multiplets due to transitions between the levels

The irregular doublet law has been fruitful in its application to the case of doublet spectra. For the system of successive elements (neutral and ionised) possessing the same structure as  $Cl_V$  the data are given in the following tables:

Table 2.—Application of irregular doublet law.

| Combination                   | Element   | $\nu$  | $\Delta\nu$ |
|-------------------------------|-----------|--------|-------------|
| $(3s^2.4s)^2S - (3s^2.4p)^2P$ | $Al_I$    | 7616   |             |
|                               | $Si_{II}$ | 15751  | 8134        |
|                               | $P_{III}$ | 23673  | 7927        |
|                               | $*S_{VI}$ | 32275  | 8597        |
|                               | $Cl_V$    | 39897  | 7622        |
| $(3s^2.3p)^2P - (3s^2.3d)^2D$ | $Al_I$    | 32325  |             |
|                               | $Si_{II}$ | 79056  | 46731       |
|                               | $P_{III}$ | 116321 | 37265       |
|                               | $S_{IV}$  | 151189 | 34869       |
|                               | $Cl_V$    | 184401 | 33202       |

\* Given by Bowen ; appears to be doubtful.

The application of the regular doublet law to these spectra is shown in Table 3. The screening constant is computed from the usual Sommerfeld formula,

$$\Delta\nu = \frac{\alpha^2 R(z-\sigma)^4}{n^3 l(l+1)}.$$

Table 3.—Screening constant and differences from Sommerfeld formula.

| Term            | Element          | $\Delta\nu$ | $\sigma$ | $\Delta\sigma$ |
|-----------------|------------------|-------------|----------|----------------|
| $(3s^2 3p)^2 p$ | $\text{Al}_I$    | 113         | 7.325    |                |
|                 | $\text{Si}_{II}$ | 287         | 6.820    | 0.505          |
|                 | $\text{P}_{III}$ | 566         | 6.453    | 0.327          |
|                 | $\text{S}_{IV}$  | 951         | 6.813    | 0.180          |
|                 | $\text{Cl}_V$    | 1491        | 6.160    | 0.153          |
| $(3s^2 4p)^2 p$ | $\text{Al}_I$    | 15          | 8.740    |                |
|                 | $\text{Si}_{II}$ | 60          | 7.976    | 0.764          |
|                 | $\text{P}_{III}$ | 136         | 7.609    | 0.367          |
|                 | $\text{S}_{IV}$  | 210         | 7.761    | -0.143         |
|                 | $\text{Cl}_V$    | 375         | 7.474    | 0.287          |

#### IV. Classification of the lines

From these tables we at once arrive at the following conclusions:

(1) The position of  $4s \leftarrow 4p$  transition is at about  $\nu$  39,000

„  $3p \leftarrow 3d$  „ „  $\nu$  185,000

„  $4p \leftarrow 4d$  „ „  $\nu$  48,000

(2) The probable separation of the terms:

$3p - 1491$ ,

$4p - 370$

$3d - 34$

With the aid of these considerations the spectrum of  $\text{Cl}_V$  is classified. Classified lines together with the term values are given in Table 4. There was practically no ambiguity in the identification of the lines. The transition  $4p \leftarrow 4d$  falls in the fluorite region, for which the data were not available.

Table 4.

| $\lambda$ | I | $\nu(\text{vac})$ | Combinations  |
|-----------|---|-------------------|---|
| 309'07    | 1 | 256364            | $(3s^2.3p)^2P_{\frac{1}{2}} - (3s^2.4s)^2S_{\frac{1}{2}}$ |
| 392'39    | 1 | 254848            | $(3s^2.3p)^2P_{\frac{3}{2}} - (3s^2.4s)^2S_{\frac{1}{2}}$ |
| 538'032   | 5 | 185863            | $(3s^2.3p)^2P_{\frac{1}{2}} - (3s^2.3d)^2D_{\frac{3}{2}}$ |
| 542'297   | 6 | 184401            | $(3s^2.3p)^2P_{\frac{3}{2}} - (3s^2.3d)^2D_{\frac{5}{2}}$ |
| 542'395   | 3 | 184367            | $(3s^2.3p)^2P_{\frac{3}{2}} - (3s^2.3d)^2D_{\frac{3}{2}}$ |
| 2205'71   | 5 | 39896'8           | $(3s^2.4s)^2S_{\frac{1}{2}} - (3s^2.4p)^2P_{\frac{3}{2}}$ |
| 2529'53   | 2 | 39521'2           | $(3s^2.4s)^2S_{\frac{1}{2}} - (3s^2.4p)^2P_{\frac{1}{2}}$ |

Terms.

|                              |                     |        |
|------------------------------|---------------------|--------|
| $(3s^2.3p)^2P_{\frac{1}{2}}$ | 562150              |        |
| $^2P_{\frac{3}{2}}$          | 560634              | 1516   |
| $(3s^2.3d)^2D_{\frac{1}{2}}$ | 376267              |        |
| $^2D_{\frac{5}{2}}$          | 376233              | 34     |
| $(3s^2.4p)^2P_{\frac{1}{2}}$ | 266265              |        |
| $^2P_{\frac{3}{2}}$          | 265889              | 376    |
| $(3s3p^2)^2D_{\frac{3}{2}}$  | 448891              |        |
| $^2D_{\frac{5}{2}}$          | 448820              | 71     |
| $^2S_{\frac{1}{2}}$          | 415507              |        |
| $^2P_{\frac{1}{2}}$          | 404219              |        |
| $^2P_{\frac{3}{2}}$          | 403257              | 962    |
| $3p^3$                       | $^4S_{\frac{3}{2}}$ | 256462 |

The term values in the spectra of  $\text{Cl}_{\text{IV}}$  and  $\text{Cl}_{\text{V}}$  were obtained by Bowen from an application of Moseley law of extrapolation of the  $(\nu/R)^{\frac{1}{2}}$  values from the preceding spectra. With data now available it is possible to apply a Rydberg formula to the two  $p$ -terms, from which the value of  $3s^23p^2P_{\frac{1}{2}}$  term, corresponding to the ionisation potential, can be calculated. For  $\text{Cl}^{\text{V}}$  this comes out to be 69'36 volts.



The older value of Bowen obtained from the application of Moseley law is 67.2 volts and is obviously too small.

### V. Spectrum of $\text{Cl}_{\text{IV}}$

The 4-valence elements in this group consist of  $\text{Si}_{\text{I}}$ ,  $\text{P}_{\text{II}}$ ,  $\text{S}_{\text{III}}$  and  $\text{Cl}_{\text{IV}}$ . The first three of this group have been analysed by Fowler,<sup>8</sup> Bowen<sup>9</sup> and Ingram,<sup>10</sup> respectively. In the case of  $\text{Cl}_{\text{IV}}$  Bowen photographed the resonance lines and the lines due to the  $pp'$  group. They will be found in Table 8. I have included them in my list because they are required for calculating the term values. These ions in their lowest state have the electron configuration  $3s^2 3p^2$ , which give rise to five low energy levels  $^3\text{P}_{0,1,2}$ ;  $^1\text{D}_2$ ;  $^1\text{S}_0$ . The next higher group of levels are from the configuration  $3s^2 3p 4s$ . The following table gives the electron configuration along with the terms arising from them. The underlined terms are those that are identified from analysis.

Table 5.

| Electron configuration     | Adopted prefix | Terms   |
|----------------------------|----------------|---|
| $1s^2 2s^2 2p^6 3s^2 3p^2$ | $3p$           | $^3\text{P}$ $^1\text{D}$ $^1\text{S}$  |
| ( ) $3s^2 3p 4s$           | $4s$           | $^3\text{P}$ $^1\text{P}$   |
| ( ) $3s 3p^3$              | $3p'$          | $^4\text{S}$ , $^3\text{D}$ , $^3\text{P}$ , $^3\text{S}$ , $^1\text{D}$ , $^1\text{P}$ |
| ( ) $3s^2 3p 3d$           | $3d$           | $^3\text{F}$ $^3\text{D}$ , $^3\text{P}$ $^1\text{F}$ $^1\text{D}$ $^1\text{P}$         |
| ( ) $3s^2 3p 4p$           | $4p$           | $^3\text{D}$ , $^3\text{P}$ , $^3\text{S}$ , $^1\text{P}$ , $^1\text{D}$ , $^1\text{S}$ |

### VI. Correlation of 3 and 4-valence systems

In the ground state of the 3-valence spectra we have two fundamental levels  $^2\text{P}_{\frac{1}{2}}$  and  $^2\text{P}_{\frac{3}{2}}$ . If an  $ms$ -electron is coupled to it these two levels split up into four, such as  $^3\text{P}_0$ ,  $^3\text{P}_1$  and  $^3\text{P}_2$ , and  $^1\text{P}_1$ . If the value of  $m$  is high it is found that two of these ( $^3\text{P}_0$  and  $^3\text{P}_1$ ) tend to converge to a limit and the other two ( $^3\text{P}_2$  and  $^1\text{P}_1$ ) to another limit, the former set corresponds to  $^2\text{P}_{\frac{1}{2}}$  and the latter set to  $^2\text{P}_{\frac{3}{2}}$ . We give below a table showing these relations in the cases under discussion.

Table 6.

|   | $\text{Si}_{\text{I}}$ | $\text{P}_{\text{II}}$ | $\text{S}_{\text{III}}$ | $\text{Cl}_{\text{IV}}$ |
|---|------------------------|------------------------|-------------------------|-------------------------|
| $ms (^3\text{P}_0 - ^3\text{P}_2)$ ; $ms (^3\text{P}_1 - ^3\text{P}_2)$         | 272; 195               | 528; 381               | 449; 494                | 1442; 10                |
| $(m+1)s (^3\text{P}_0 - ^3\text{P}_2)$ ; $(m+1)s (^3\text{P}_1 - ^3\text{P}_2)$ | 281; 214               | 546; 435               | 925; 772                | ...                     |
| $(m+1)s (^3\text{P}_0 - ^3\text{P}_2)$ ; $(m+2)s (^3\text{P}_1 - ^3\text{P}_2)$ | 284; 231               | ...                    | ...                     | ...                     |
| Limit $^2\text{P}_{\frac{1}{2}}$ - $^2\text{P}_{\frac{3}{2}}$ for $\text{M}^+$  | 287                    | 566                    | 951                     | 1516                    |

Following Goudsmidt and Humphreys<sup>11</sup> it can be shown that where Russell-Saunders coupling is operative the  $(3s^2 3p 4s) {}^3P$  separations should be smaller than those of  $(3s^2 3p) {}^2P$ . But the total  $(3s^2 3p 4p)$  P-separations will not be affected. As is known from other spectra higher nuclear charge is favourable to a change of coupling from the Russell-Saunders type to the  $(jj)$  type. Thus the  $s^2 ps$  configuration with Russell-Saunders coupling gives  ${}^3P$  and  ${}^1P$  terms. When we go over to limiting  $(jj)$  coupling we still have 4 levels characterised by the same inner quantum values, but two of them having values 0, 1 lie relatively close together and are separated by the  $(3s^2 3p) {}^2P$  interval of the next ion from the two having the  $j$ -values 2 and 1. Without going into rules of correlation in detail, it may be stated that the levels of corresponding  $j$ -values in the  $(RS)$ -coupling go over to the new levels in such a way that the connecting lines do not cross. (For detail see the forthcoming paper on the spectrum of Iodine in the Proc. Roy. Soc. Lond.). Consequently, while the triplet interval may change we do not expect a change in the total  $(3s^2 3p 4p)$  P-separation, but rather expect the former to approach the latter as a limit. This consideration enabled me to establish the  ${}^1P_1$  interval from the  ${}^3P$ 's.

### VII. Location of the multiplets ( $3p 4s \leftarrow 3p 4p$ )

The most fruitful rules for location of any multiplet are the irregular doublet law, discussed in the case of  $Cl_V$ , and the horizontal comparison law of Saha and Majumdar.<sup>12</sup> The irregular doublet law is obeyed by the triplets in these spectra ( $Si_I$ ,  $P_{II}$ ,  $S_{III}$ ,  $Cl_{IV}$ ) in an unimpeachable manner as will be seen from Table 7. In all cases the smoothest of the differences are unbroken.

Table 7.

| Element   | $3p {}^2 3P_2 - 3p 3d {}^3 D_3$ | $\Delta \nu$ | $3p 4s {}^3 P_2 - 3p 4p {}^3 P_2$ | $\Delta \nu$ |
|-----------|---------------------------------|--------------|-----------------------------------|--------------|
| $Si_I$    | 54033                           |              | ...                               |              |
| $P_{II}$  | 103726                          | 49693        | 18425                             |              |
| $S_{III}$ | 142295                          | 38569        | 26045                             | 7620         |
| $Cl_{IV}$ | 165401                          | 23106        | 33416                             | 7317         |

Application of horizontal comparison method is difficult in this case since the analysis of only two of the series  $S_{IV}$ ,  $Cl_{IV}$ ,  $A_{IV}$ ,  $K_{IV}$ ,  $Ca_{IV}$ ,  $Sc_{IV}$  and  $Ti_{IV}$  are known. They are  $S_{IV}$ , and  $Ti_{IV}$ . The transition  $3p^2 4s \leftarrow 3p^2 4p$  in the case of  $S_{IV}$  gives out the line 31065, and in the transition  $4s \leftarrow 4p$  in  $Ti_{IV}$  the corresponding line is 48396. The law says that the centre of gravity of  $4s \leftarrow 4p$  transitions of all the spectra given by  $Cl_{IV}$ ,  $A_{IV}$  . . . etc. should form a linear sequence. Extrapolating in this way, the centre of gravity of  $4s \leftarrow 4p$  transition of  $Cl_{IV}$  comes out at about

$\nu$  34,000  $\text{cm}^{-1}$ . This value is in good agreement with that obtained with the aid of the irregular doublet law.

The transition  $4p \leftarrow 4d$  can also be located in a similar way. As this transition falls beyond the range of the data available to us we need not consider it in detail.

### VIII. Classification of the lines, and the term values of $\text{Cl}_{\text{IV}}$ spectrum

The classified lines and the approximate term values are given in Table 8 below. This table includes also the lines in the Schumann region photographed by Bowen and classified for the transition  $3p \leftarrow 4s$ .

Table 8.

| $\lambda$ | $l$ | $\nu_{(\text{vac})}$ | Combination         | Terms                       | $\Delta\nu$ |
|-----------|-----|----------------------|---------------------|-----------------------------|-------------|
| 463.011   | 3   | 215978               | $3p^3P_1 - 4s^3P_2$ | $3s^2 3p^2 {}^3P_0$ 447123  | 490         |
| 464.292   | 3   | 215332               | $3p^3P_0 - 4s^3P_1$ | ${}^3P_1$ 446633            |             |
| 464.861   | 4   | 215118               | $3p^3P_2 - 4s^3P_2$ | ${}^3P_2$ 445785            | 848         |
| 465.350   | 3   | 214892               | $3p^3P_1 - 4s^3P_1$ | ${}^3P_2$ 445785            |             |
| 466.132   | 3   | 214532               | $3p^3P_1 - 4s^3P_0$ | $3s^2 3p 4s {}^3P_0$ 232101 | 364         |
| 467.194   | 3   | 214044               | $3p^3P_2 - 4s^3P_1$ | ${}^3P_1$ 231737            |             |
| 2651.77   | 2   | 37699.5              | $4s^3P_1 - 4p^1S_0$ | ${}^3P_1$ 231737            | 1078        |
| 2729.57   | 1   | 36624.9              | $4s^3P_0 - 4p^3S_1$ | ${}^3P_2$ 230659            |             |
| 2756.86   | 2   | 36262.4              | $4s^3P_1 - 4p^3S_1$ | ${}^1P_1$ 229135            | 346         |
| 2841.56   | 3   | 35181.6              | $4s^3P_2 - 4p^3S_1$ | ${}^3D_1$ 202684            |             |
| 2848.36   | 2   | 35097.6              | $4s^1P_1 - 4p^1S_0$ | ${}^3D_2$ 202338            | 504         |
| 2898.29   | 3   | 34493.0              | $4s^3P_1 - 4p^3P_2$ | ${}^3D_3$ 201834            |             |
| 2933.86   | 1   | 34074.8              | $4s^3P_0 - 4p^3P_1$ | ${}^1P_1$ 200045            | 424         |
| 2965.45   | 3   | 33711.9              | $4s^3P_1 - 4p^3P_1$ | ${}^3P_0$ 198448            |             |
| 2970.42   | 2   | 33655.5              | $4s^1P_1 - 4p^3S_1$ | ${}^3P_1$ 198024            | 780         |
| 2991.67   | 4   | 33416.4              | $4s^3P_2 - 4p^3P_2$ | ${}^3P_2$ 197244            |             |
| 3003.18   | 1   | 33288.4              | $4s^3P_1 - 4p^3P_0$ | ${}^3S_1$ 195478            | 194038      |
| 3063.17   | 2   | 32636.5              | $4s^3P_2 - 4p^3P_1$ | ${}^1S_0$ 194038            |             |
| 3178.76   | 1   | 32054.8              | $4s^3P_0 - 4p^3P_1$ |                             |             |
| 3184.65   | 2   | 31892.3              | $4s^1P_1 - 4p^3P_2$ |                             |             |
| 3154.39   | 0   | 31692.7              | $4s^3P_1 - 4p^1P_1$ |                             |             |
| 3213.24   | 1   | 31112.3              | $4s^1P_1 - 4p^3P_1$ |                             |             |
| 3257.73   | 1   | 30687.4              | $4s^1P_1 - 4p^3P_0$ |                             |             |
| 3265.44   | 2   | 30615.0              | $4s^3P_2 - 4p^3P_1$ |                             |             |
| 3398.20   | 2   | 29418.9              | $4s^3P_0 - 4p^3D_1$ |                             |             |
| 3400.38   | 3   | 29400.3              | $4s^3P_1 - 4p^3D_2$ |                             |             |
| 3436.44   | 3   | 29091.6              | $4s^1P_1 - 4p^1P_1$ |                             |             |
| 3440.90   | 2   | 29053.9              | $4s^3P_1 - 4p^3D_1$ |                             |             |
| 3468.23   | 4   | 28834.9              | $4s^3P_2 - 4p^3D_3$ |                             |             |
| 3530.04   | 2   | 28320.2              | $4s^3P_2 - 4p^3D_2$ |                             |             |
| 3573.66   | 1   | 27974.6              | $4s^3P_2 - 4p^3D_1$ |                             |             |
| 3731.80   | 2   | 26796.3              | $4s^1P_1 - 4p^3D_2$ |                             |             |
| 3779.35   | 2   | 26452.1              | $4s^1P_1 - 4p^3D_1$ |                             |             |
| 4096.98   | 1   | 24401.4              | $4s^3P_2 - 4p^1D_1$ |                             |             |
| 4369.60   | 2   | 22879.0              | $4s^1P_1 - 4p^1D_2$ |                             |             |

The term values are obtained by assuming that corresponding terms in  $3s^2 3p^2$  and  $3s^2 4p^2$  follow Rydberg sequences. Thus the ground term  $3s^2 3p^2 {}^3P$  of  $\text{Cl}_{\text{IV}}$  to be 447123  $\text{cm}^{-1}$ . The ionisation potential of  $\text{Cl}_{\text{IV}}$  thus comes out to be 55.17 volts. The value given by Bowen for  $\text{Cl}_{\text{IV}}$  is 47.6 volts. This value is too

low since the I.P. of  $S_{IV}$ , the preceding element, which must be much less than that of  $Cl_{IV}$ , is given by Bowen to be 47.3 volts.

In conclusion I wish to thank Prof. M. N. Saha, F.R.S., for his kind help in preparing this paper.

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## ON THE SINGULARITIES OF LAPLACE-ABEL INTEGRAL

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1. The object of this paper is to obtain certain generalizations of Polya's results<sup>1</sup> concerning the singularities of the Laplace-Abel integral

$$f(s) = \int_0^{\infty} \phi(z) e^{-sz} dz,$$

where  $\phi(z)$  is an analytic function of  $z$  of exponential type. Polya assumes  $\phi(z)$  to be an integral function of  $z$  while we take  $\phi(z)$  to be an analytic function of  $z$  in the angular region  $|\arg z| \leq \alpha$ , where  $\alpha > 0$ . For simplicity, we take  $\alpha \leq \frac{\pi}{2}$ . Our first three theorems establish reciprocal relations between  $\phi(z)$  and  $f(z)$  similar to those established by Polya in §§ 21-22 of his memoir referred to above, and our theorem IV is a generalization of Polya's result established on page 585. Our theorem V is a generalization of a lemma of Prof. Hardy. An abstract of this paper has appeared in the Comptes Rendus, Tome 194, N° 24.

2. THEOREM I.—If  $\phi(z)$  is an analytic function of  $z (= \rho e^{i\psi})$  of exponential type in the angle  $|\psi| \leq \alpha$ , and

$$(2.1) \quad \lambda(\psi) \equiv \lim_{\rho \rightarrow \infty} \frac{\log |\phi(\rho e^{i\psi})|}{\rho} \text{ is not negative for } |\psi| < \alpha;$$

$$(2.2) \quad \phi(0) = 0;$$

then

$$(2.3) \quad f(s) = \int_0^{\infty} \phi(z) e^{-sz} dz$$

is an analytic function of  $s$  in the region lying exterior to the curve  $\Sigma$  associated with  $\phi(z)$  in a particular manner, and further  $f(s) = O\left(\frac{1}{|s|^2}\right)$  in the region of its regularity.

The integral (2.3) is absolutely and uniformly convergent in the half plane  $\sigma \geq k + \delta > k$ , where  $\delta$  is any arbitrary positive number, and  $k$  is the maximum value of  $\lambda(\psi)$  in the range  $-\alpha < \psi < \alpha$ . Hence,  $f(s)$  is an analytic function of  $s$  at least in the half plane  $\sigma \geq k + \delta > k$ .

Now, suppose for a moment, that  $s (= \sigma + it)$  lies in the region  $\sigma > k + \delta$  and  $t < -(k + \delta)$ . Then

$$(2.4) \quad \int_0^{\infty(\psi)} \phi(z) e^{-sz} dz = \int_0^{\infty(\psi)} \phi(z) e^{-sz} dz, \quad (0 \leq \psi \leq \alpha),$$

$$\text{since} \quad \left| \int_0^{\psi} \phi(\rho e^{i\theta}) e^{-s\rho e^{i\theta}} \rho e^{i\theta} d\theta \right| \rightarrow 0 \text{ as } \rho \rightarrow \infty.$$

Now, since

$$\int_0^{\infty(\psi)} |\phi(z) e^{-sz}| dz \leq \int_0^{\infty} e^{(\lambda(\psi) + \epsilon - \sigma \cos \psi + t \sin \psi) \rho} d\rho,$$

which is uniformly convergent in the region

$$(2.5) \quad \sigma \cos \psi - t \sin \psi \geq \lambda(\psi) + \epsilon' > \lambda(\psi), \quad (\epsilon' > \epsilon, 0 \leq \psi \leq \alpha),$$

the integral on the right hand side of (2.4) is absolutely and uniformly convergent in the region (2.5), and so represents there an analytic function of  $s$ . The same result holds when  $\psi$  lies between  $-\alpha$  and  $\beta$ .

By the principle of analytic continuation it follows, therefore, that the function  $f(s)$  defined initially by (2.3) in a certain half-plane is analytic in a much wider region, namely, the region lying exterior to the curve\*  $\Sigma$  which is the envelope of the lines

$$(2.6) \quad \sigma \cos \psi - t \sin \psi = \lambda(\psi), \quad (|\psi| \leq \alpha)$$

Now, if we can prove that the order of  $f(s)$  in this region, when  $s$  is sufficiently away from  $\Sigma$ , is  $\left(\frac{1}{|s|^2}\right)$ , then its order throughout the region (2.5) will be the same, since this region does not include the origin, which lies on or to the left of  $\Sigma$ .

If  $s$  lies in the region of regularity of  $f(s)$  and is sufficiently away from the curve  $\Sigma$ , then choosing the value of  $\psi$  appropriately, we have

$$(2.7) \quad f(s) = \int_0^{\infty(\psi)} \phi(z) e^{-sz} dz \\ = \left[ -\phi(z) \frac{e^{-sz}}{s} \right]_0^{\infty(\psi)} + \frac{1}{s} \int_0^{\infty(\psi)} \phi'(z) e^{-sz} dz$$

\* By the well-known properties of  $\lambda(\psi)$  and the assumption (2.1),  $\Sigma$  is a convex curve, the origin lying on or inside it. It is known that  $\lambda'(\psi)$  possesses discontinuities of the first kind only and to these correspond straight pieces on the curve  $\Sigma$ .



$$\begin{aligned}
&= \frac{1}{s} \int_0^{\infty(\psi)} \phi'(z) e^{-sz} dz \\
&= \left[ \frac{-\phi'(z) e^{-sz}}{s^2} \right]_0^{\infty(\psi)} + \frac{1}{s^2} \int_0^{\infty(\psi)} \phi''(z) e^{-sz} dz \\
&= O\left(\frac{1}{|s|^2}\right),
\end{aligned}$$

since  $\phi(0) = 0$ , and  $|\phi(z) e^{-sz}|$  and  $|\phi'(z) e^{-sz}|$  both  $\rightarrow 0$  as  $|z| \rightarrow \infty$  along the radius vector  $\psi$ ,  $\phi'(z)$  being of order  $e^{(k+\epsilon)\rho}$ .

3. Now we establish the converse of Theorem I.

**THEOREM II.**—If  $f(s)$  is analytic in the region lying exterior to the curve  $\Sigma$  (defined as in theorem I), and is equal to  $O\left(\frac{1}{|s|^2}\right)$ , then there exists a function

$$(3.1) \quad \phi(z) = \frac{1}{2\pi i} \int_{\Sigma'} f(s) e^{zs} ds,$$

$\Sigma'$  being a curve to the right of and parallel to  $\Sigma$  at a distance  $\epsilon'$ , such that  $\phi(z)$  is analytic in the angle  $|\psi| \leq \alpha$ , of order  $e^{\{\lambda(\psi) + \epsilon\}\rho}$ , and vanishes at the origin, and further

$$f(s) = \int_0^{\infty} \phi(z) e^{-sz} dz.$$

Now,

$$\begin{aligned}
\frac{1}{2\pi i} \int_{\Sigma'} f(s) e^{zs} ds &= \frac{1}{2\pi i} \left\{ \int_{L_1} f(s) e^{zs} ds + \int_{L_2} f(s) e^{zs} ds \right. \\
&\quad \left. + \int_{L_3} f(s) e^{zs} ds \right\},
\end{aligned}$$

where  $L_2$  is a finite portion of the curve  $\Sigma'$ , and  $L_1$  and  $L_3$  are portions of  $\Sigma'$  extending to infinity whose equations are

$$\sigma \cos \alpha - t \sin \alpha = \lambda(\alpha) + \epsilon',$$

and

$$\sigma \cos \alpha + t \sin \alpha = \lambda(-\alpha) + \epsilon' \text{ respectively.}$$

$$\left| \int_{L_1} f(s) e^{zs} ds \right| \leq \int_{-\infty}^a |f(s)| e^{\rho(\sigma \cos \Psi - t \sin \Psi)} \sqrt{1 + \left(\frac{dt}{d\sigma}\right)^2} d\sigma$$

$$\begin{aligned}
&= \int_{-\infty}^a \left\{ \left| f(s) \right| e^{\frac{\rho\sigma}{\sin a} \left[ \cos \psi \sin a - \sin \psi \cos a \right]} \right. \\
&\quad \left. e^{\frac{\rho \sin \psi}{\sin a} (\lambda(a) + \epsilon')} \sqrt{1 + \left( \frac{dt}{d\sigma} \right)^2} d\sigma \right. \\
&\quad \left. \leq K \int_{-\infty}^a \frac{1}{|s|^2} e^{\frac{\rho\sigma}{\sin a} \sin(a - \psi)} d\sigma, \right.
\end{aligned}$$

where  $a$  is finite and  $K$  is a constant. The last integral will be convergent provided  $\sin(a - \psi) \geq 0$ , i.e.,  $\psi \leq a$ .

Similarly  $\int_{L_3} \left| f(s) e^{zs} ds \right|$  is convergent provided  $\psi > -a$ .

Hence, the integral (3.1) is absolutely and uniformly convergent in the angular region  $|\psi| \leq a$ , and so  $\phi(z)$  represents an analytic function of  $z$  in this angular region.

To obtain a superior limit of  $|\phi(z)|$ , we observe that

$$\begin{aligned}
|\phi(z)| &\leq \frac{1}{2\pi} \left\{ \int_{L_1} |f(s)| e^{\rho(\sigma \cos \psi - t \sin \psi)} \sqrt{1 + \left( \frac{d\sigma}{dt} \right)^2} dt \right. \\
&\quad + \int_{L_2} |f(s)| e^{\rho(\sigma \cos \psi - t \sin \psi)} \sqrt{1 + \left( \frac{d\sigma}{dt} \right)^2} dt \\
&\quad \left. + \int_{L_3} |f(s)| e^{\rho(\sigma \cos \psi - t \sin \psi)} \sqrt{1 + \left( \frac{d\sigma}{dt} \right)^2} dt \right\}
\end{aligned}$$

Now, expressions under the radical signs in each case = 0 (1), and also  $|f(s)|$  is bounded over  $\Sigma'$ . Thus the determination of a superior limit of  $|\phi(z)|$  depends upon the maximum value of  $e^{\rho(\sigma \cos \psi - t \sin \psi)}$  over the path of integration, which is the envelope of the lines (2.5). From this equation we see that given any particular value of  $\psi$ , say  $\psi_1$ , the expression  $\sigma \cos \psi_1 - t \sin \psi_1$ , can at most be equal to  $\lambda(\psi_1) + \epsilon'$  for any point  $s$  on  $\Sigma'$ . To prove this we observe as follows:

The line

$$(3.3) \quad \sigma \cos \psi_1 - t \sin \psi_1 - [\lambda(\psi_1) + \epsilon'] = 0$$

is a tangent to  $\Sigma'$ , which lies wholly on the same side of it as the origin. Therefore, the expression on the left side of equation (3.3) is negative for all points of  $\Sigma'$ , except those which are common to the line (3.3), for which it is zero. Hence, the maximum value of  $\sigma \cos \psi_1 - t \sin \psi_1$  on  $\Sigma'$  is actually  $\lambda(\psi_1) + \epsilon'$ .

Consequently  $|\phi(z)| \leq e^{-\rho(\lambda(\psi_1) + \epsilon'')} \text{ for } \rho \geq \rho_0(\epsilon''), \quad (\epsilon'' > \epsilon').$

Now

$$(3.4) \quad \phi(0) = \frac{1}{2\pi i} \int_{\Sigma'} f(s) ds.$$

The path of integration can be replaced by the arc of a circle of infinite radius lying to the right of  $\Sigma'$ ; and since  $|sf(s)| \rightarrow 0$  as  $|s| \rightarrow \infty$ , the value of the integral (3.4) is zero, and so  $\phi(0) = 0$ .

It is easy to prove that for  $z$  real and positive

$$\begin{aligned} \phi(z) &= \frac{1}{2\pi i} \int_{\Sigma} f(s) e^{zs} ds, \\ &= \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} f(s) e^{zs} ds, \end{aligned}$$

where  $c > \lambda(0)$ .

Suppose  $R(\xi) > c$ . Then

$$\begin{aligned} \int_0^\infty \phi(z) e^{-\xi z} dz &= \frac{1}{2\pi i} \int_0^\infty e^{-\xi z} \int_{c-i\infty}^{c+i\infty} e^{zs} f(s) ds dz \\ &= \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} f(s) \int_0^\infty e^{-z(\xi-s)} dz ds \\ (3.5) \quad &= \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} \frac{f(s) ds}{\xi-s} \end{aligned}$$

since  $\int_0^\infty \int_{c-i\infty}^{c+i\infty} |f(s) e^{-z(\xi-s)} dz| ds$  is convergent.

Now  $\left| \frac{sf(s)}{\xi-s} \right| \rightarrow 0$  as  $|s| \rightarrow \infty$ , and hence we can add to the contour of the integral (3.5) an arc of a circle of infinite radius lying to the right of the line  $R(s) = c$ . Consequently,

$$\int_0^\infty \phi(z) e^{-\xi z} dz = f(\xi).$$

4. In theorem II we have proved that if  $f(s)$  be given satisfying certain conditions, then there is an analytic function

$$(4.1) \quad \phi(z) = \frac{1}{2\pi i} \int_{\Sigma'} f(s) e^{zs} ds$$

such that

$$(4.2) \quad f(s) = \int_0^{\infty} \phi(z) e^{-sz} dz,$$

Now we wish to show that  $\phi(z)$  is the only analytic function of its kind which will satisfy the equation (4.2).

Suppose, if possible, that there is another analytic function  $\phi_1(z)$  satisfying conditions similar to (2.1) and (2.2), which satisfies the equation (4.2). Then we will show that  $\phi_1(z) \equiv \phi(z)$  as defined by (4.1).

To prove this we need only show that  $\phi_1(z) = \phi(z)$  for some real and positive values of  $z$ .

Now, as in § 3,

$$\begin{aligned} \phi(z) &= \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} f(s) e^{zs} ds = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} e^{zs} \int_0^{\infty} \phi_1(t) e^{-st} dt ds \\ &= \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} e^{zs} \left[ \int_0^R e^{-st} \phi_1(t) dt + \int_R^{\infty} e^{-st} \phi_1(t) dt \right] ds, \end{aligned}$$

where  $R$  is arbitrary and greater than  $z$ , and the line  $\sigma=c$  lies in the region of regularity of  $f(s)$  as well as in that of  $\phi_1(s)$  to be defined presently.

The second integral will be proved to be zero, and the first equal to  $\phi_1(z)$ .

Putting  $u=t-R$ , we get

$$\int_R^{\infty} e^{-st} \phi_1(t) dt = e^{Rs} \int_0^{\infty} e^{-su} \phi_1(u+R) du = e^{Rs} f_1(s), \text{ say.}$$

$f_1(s)$  is an analytic function of  $s$  on the line  $\sigma=c$  and in the half-plane lying to its right, and is of order  $\left(\frac{1}{|s|}\right)$  in the region.

Now we consider

$$(4.3) \quad \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} f_1(s) e^{(z-R)s} ds.$$

Let us study the integral  $\int e^{s(z-R)} f_1(s) ds$  extended over the rectangle whose vertices are  $c-i\gamma$ ,  $d-i\gamma$ ,  $d+i\gamma$ , and  $c+i\gamma$ , ( $d > c$ )

$$\left| \int_{d-i\gamma}^{d+i\gamma} e^{s(R-z)} f_1(s) ds \right| \leq K_1 \int_{-\gamma}^{\gamma} \frac{e^{-d(R-z)}}{\sqrt{d^2 + \gamma^2}} d\gamma, (K_1 \text{ const.})$$

and this  $\rightarrow 0$  as  $d \rightarrow \infty$ ,  $\gamma$  remaining fixed.

Hence

$$(4.4) \quad \int_{c-i\gamma}^{c+i\gamma} e^{-s(R-z)} f_1(s) ds = \int_{c-i\gamma}^{\infty-i\gamma} e^{-s(R-z)} f_1(s) ds - \int_{c+i\gamma}^{\infty+i\gamma} e^{-s(R-z)} f_1(s) ds,$$

provided the last two integrals exist.

Now

$$\begin{aligned} \left| \int_{c-i\gamma}^{\infty-i\gamma} e^{-s(R-z)} f_1(s) ds \right| &\leq K_1 \int_c^{\infty} \frac{e^{-\sigma(R-z)}}{\sqrt{\sigma^2 + \gamma^2}} d\sigma \\ &< \frac{K_1}{\gamma} \int_c^{\infty} e^{-\sigma(R-z)} d\sigma \end{aligned}$$

which  $\rightarrow 0$  as  $\gamma \rightarrow \infty$ .

Similarly the second member on the right hand side of (4.4) tends to 0 as  $\gamma \rightarrow \infty$ .

Consequently the integral (4.3) is zero.

$$\text{Now consider } \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} e^{zs} \int_0^R e^{-st} \phi_1(t) dt ds.$$

$$\text{It is equal to } \lim_{\gamma \rightarrow \infty} \frac{1}{2\pi i} \int_0^R \phi_1(t) \int_{c-i\gamma}^{c+i\gamma} e^{s(z-t)} ds dt.$$

$$= \lim_{\gamma \rightarrow \infty} \frac{2i}{2\pi i} \int_0^R \phi_1(t) e^{\frac{c(z-t)}{z-t}} \sin \gamma(z-t) dt.$$

This is Fourier's integral,<sup>2</sup> and its value is  $\phi_1(z)$ , since  $\phi_1(t)$  is an analytic function of  $t$ . That is,  $\phi(z) \equiv \phi_1(z)$ .

We have thus established the uniqueness of  $\phi(z)$ , that is we have proved the following theorem:—

**THEOREM III.**—*Given a function  $f(s)$  satisfying certain specified conditions, there is only one analytic function satisfying conditions (2.1) and (2.2), which can satisfy the equation (2.3).*

**COROLLARY.**—*Two different functions  $\phi_1(z)$  and  $\phi_2(z)$  cannot give rise to two functions  $f_1(s)$  and  $f_2(s)$  differing by a constant.*

Suppose, if possible,

$$\begin{aligned} f_1(s) - f_2(s) &= K_2 = \int_0^{\infty} [\phi_1(z) - \phi_2(z)] e^{-sz} dz \\ &= \int_0^{\infty} \phi_3(z) e^{-sz} dz, \quad [\phi_3(z) = \phi_1(z) - \phi_2(z)]. \end{aligned}$$

By virtue of theorem I the last integral must represent a function of order  $\left(\frac{1}{|s|^2}\right)$  which will vanish at infinity, and so  $f_1(s)$  and  $f_2(s)$  cannot differ by a non-zero constant.

**5. THEOREM IV.**—*If  $\phi(z)$  satisfies (2.1) and (2.2), then  $f(s)$  is an analytic function of  $s$  outside  $\Sigma$ , and every tangent enveloping  $\Sigma$  is a line of absolute convergence*

*of the integral  $\int_0^{\infty(\psi)} \phi(z) e^{-sz} dz$ , and has at least one singular point of  $f(s)$  lying on it.*

Suppose, if possible, the point P (or points), at which the line  $\sigma \cos \psi - t \sin \psi = \lambda(\psi)$  for any particular value of  $\psi$ , say  $\psi_1$ , touches  $\Sigma$  is an ordinary point of  $f(s)$ . We can replace the portion of the curve  $\Sigma$  in the neighbourhood of the point P (or points) by a straight piece, say L, parallel to and at a small distance  $\delta$  from the tangent at P, the line L being on the same side of the tangent as the centre of curvature of the curve, so that  $f(s)$  is analytic outside the curve  $\Sigma'$  which is only the curve  $\Sigma$  as deformed by L in the neighbourhood of P. Evidently  $\Sigma'$  also is a convex curve. By virtue of the previous theorems, we have

$$\phi(z) = \frac{1}{2\pi i} \int_{\Sigma''} f(s) e^{zs} ds,$$

where  $\Sigma''$  is a curve parallel to  $\Sigma'$  at an arbitrarily small distance  $\epsilon'$  on the side of the point P (or points), where  $\epsilon' < \delta$ . The equation of the portion of  $\Sigma''$  corresponding to the straight piece L of  $\Sigma'$  is

$$\sigma \cos \psi_1 - t \sin \psi_1 = \lambda(\psi_1) - \delta + \epsilon'.$$

Arguing as in theorem II, we see that the maximum value of  $|\phi(z)|$  for  $\psi = \psi_1$  depends upon the maximum value of  $\sigma \cos \psi_1 - t \sin \psi_1$  for points on  $\Sigma''$  which can at most be equal to  $\lambda(\psi_1) - \delta + \epsilon'$ . That is to say,

$$(5.1) \quad |\phi(z)| < e^{\{\lambda(\psi_1) - (\delta - \epsilon'')\}\rho}, \text{ for } \rho \geq \rho'(\epsilon''),$$

where  $\epsilon''$  is a small quantity greater than  $\epsilon'$  but less than  $\delta$ , by a proper choice of the arbitrary  $\epsilon'$ .

But the asymptotic equality (2.1) implies two inequalities

$$(5.2) \quad |\phi(z)| < e^{\rho[\lambda(\psi) + \epsilon]} \text{ for every } \epsilon > 0 \text{ and } \rho \geq \rho_0(\epsilon), \text{ and}$$

$$(5.3) \quad |\phi(z)| > e^{\rho[\lambda(\psi) - \epsilon]} \text{ for a corresponding sequence of values of } \rho \text{ whose limit is infinity.}$$

As the conditions (5.1) and (5.3) are contradictory, the point P or the points of contact of the tangent with  $\Sigma$ , cannot all be ordinary points of  $f(s)$ . This establishes our theorem.

6. Now we give a generalization of a lemma of Prof. Hardy.<sup>3</sup>

**THEOREM V.**—*A necessary and sufficient condition that  $\phi(z)$  be an analytic function of  $z$  in the angle  $|\psi| \leq \alpha$ , vanish at the origin, and satisfy the asymptotic equality*

$$(6.1) \quad \lim_{\rho \rightarrow \infty} \frac{\log |\phi(\rho e^{i\psi})|}{\rho} = \lambda(\psi) \quad \text{for } |\psi| \leq \alpha,$$

*when  $\lambda(\psi) \geq 0$ , and is such that the envelope of the lines  $\sigma \cos \psi - t \sin \psi = \lambda(\psi)$  is a convex curve, is that it should be of the form*

$$(6.2) \quad \phi(z) = \frac{1}{2\pi i} \int_{\Sigma'} f(s) e^{zs} ds,$$

*where  $f(s)$  is analytic in the region lying exterior to  $\Sigma$ , but not in any more extensive region of the same character,  $\Sigma'$  being a curve parallel to  $\Sigma$  at an arbitrarily small distance  $\epsilon$  towards its right.*

That the condition is necessary follows by a successive application of theorems I, II and III, and by observing that as a consequence of theorem IV every tangent to  $\Sigma$  contains at least one singular point of  $f(s)$ .

Everything as regards the sufficiency of the condition follows easily from the formula (6.2) excepting the asymptotic behaviour of  $\phi(z)$ . All that it establishes is that

$$(6.3) \quad \lim_{\rho \rightarrow \infty} \frac{\log |\phi(\rho e^{i\psi})|}{\rho} \leq \lambda(\psi).$$

It is easy to show that the sign of inequality in (6.2) is inadmissible. Suppose for  $\psi = \psi_1$ , we have  $\lim_{\rho \rightarrow \infty} \frac{\log |\phi(\rho e^{i\psi_1})|}{\rho} \equiv h < \lambda(\psi_1)$ .

Then as in theorem I,  $f(s)$  can be proved to be regular in the half-plane  $\sigma \cos \psi_1 - t \sin \psi_1 > h$ , which is greater than the half-plane

$$\sigma \cos \psi_1 - t \sin \psi_1 > \lambda(\psi_1).$$

But this is contrary to the hypothesis that  $f(s)$  is not analytic in a more extensive region than the one lying exterior to  $\Sigma$ . Hence,

$$\lim_{\rho \rightarrow \infty} \frac{\log |\phi(\rho e^{i\psi})|}{\rho} = \lambda(\psi).$$

7. In proving the foregoing theorems we have assumed (a)  $\alpha \leq \frac{\pi}{2}$ , (b)  $\phi(0) = 0$  and (c)  $\lambda(\psi)$  is not negative for any value of  $\psi$ . Now, so far as the study of the singularities of  $f(s)$ , defined initially by (2.3), is concerned all these restrictions can be removed.

(a) If  $\alpha > \frac{\pi}{2}$ ,  $\Sigma$  will be a closed curve and  $f(s)$  will be analytic in the region lying exterior to  $\Sigma$  when a cut has been drawn in it.

(b) If  $\phi(0) = c \neq 0$ , then

$$\begin{aligned} f(s) &= \int_0^{\infty} [c + \phi(z) - c] e^{-sz} dz \\ &= \int_0^{\infty} c e^{-sz} dz + \int_0^{\infty} \phi_1(z) e^{-sz} dz \\ &= \frac{c}{s} + f_1(s), \end{aligned}$$

so that the singularities of  $f(s)$  can be ascertained from those of  $f_1(s)$ .

(c) So far as the study of the singularities of  $f(s)$  is concerned, restriction (2.1) is immaterial. For, let  $\lambda(\psi)$  be negative for some values of  $\psi$ . By applying the linear transformation  $s = s' - (\alpha + i\beta)$  to the equation (2.3), we have

$$\begin{aligned} f[s' - (\alpha + i\beta)] &= f_1(s') = \int_0^{\infty} \phi(z) e^{(\alpha + i\beta)z} e^{-s'z} dz \\ &= \int_0^{\infty} \phi_1(z) e^{-s'z} dz \end{aligned}$$



where  $\alpha, \beta$  can be so chosen as to make  $\phi_1(z)$  conform to the condition (2.1). We get a curve  $\Sigma'$  in the  $s'$ -plane, having the origin on or inside it, by means of which we can study the singularities of  $f_1(s')$ . Then the curve in the  $s$ -plane corresponding to  $\Sigma'$  in the  $s'$ -plane gives the singularities of  $f(s)$ .

8. Now we are in a position to deduce a number of results from the foregoing theorems.

(a) Two different functions  $\phi_1(z)$  and  $\phi_2(z)$  of exponential type and analytic in the region  $|\psi| \leq \alpha, \alpha > \frac{\pi}{2}$  cannot give rise to two functions  $f_1(s)$  and  $f_2(s)$  which will differ by an integral function.

Suppose

$$f_1(s) = \int_0^{\infty} \phi_1(z) e^{-sz} dz,$$

and 
$$f_2(s) = \int_0^{\infty} \phi_2(z) e^{-sz} dz,$$

so that 
$$f_1(s) - f_2(s) = f_3(s) = \int_0^{\infty} \phi_3(z) e^{-sz} dz,$$

where 
$$\phi_3(z) \equiv \phi_1(z) - \phi_2(z).$$

Now  $f_3(s)$  is analytic outside a closed curve  $\Sigma$  when a cut has been drawn in the  $s$ -plane and its order is  $\left(\frac{1}{|s|}\right)$  in the region of its regularity.

But by assumption  $f_3(s)$  is an integral function and so the cut disappears. By virtue of the order of  $f_3(s)$  we find  $f_3(s) \equiv 0$ . This means that  $\phi_1(z)$  and  $\phi_2(z)$  are identical functions, which contradicts our hypothesis.

(b) If  $f_1(s)$  and  $f_2(s)$  be defined by

$$f_1(s) = \int_0^{\infty} \phi(a+z) e^{-sz} dz, \text{ and}$$

$$f_2(s) = \int_0^{\infty} \phi(b+z) e^{-sz} dz,$$

where  $\phi(z)$  is an analytic function of  $z$  in the region  $|\psi| \leq \alpha$ , and the points  $a$  and  $b$  lie in this region, then  $f_1(s)$  and  $f_2(s)$  have the same line of absolute convergence, and the same singularities.

To prove this we need only observe that

$$f_1(s) = \int_0^{\infty} \phi(z+a) e^{-sz} dz = e^{as} \int_a^{\infty} \phi(u) e^{-su} du,$$

$$\text{and } f_2(s) = \int_0^{\infty} \phi(z+b) e^{-sz} dz = e^{bs} \int_b^{\infty} \phi(u) e^{-su} du,$$

$$\text{so that } e^{-as} f_1(s) - e^{-bs} f_2(s) = \int_b^a \phi(u) e^{-su} du = \text{an integral function of } s.$$

The above is a generalization of a result due to Polya.\*

(c) Suppose the functions  $f_1(s)$  and  $f_2(s)$  are defined by the series

$$f_1(s) = \sum_0^{\infty} \phi(a+n) e^{-sn} \text{ and } f_2(s) = \sum_0^{\infty} \phi(b+n) e^{-sn}$$

respectively, where  $\phi(z)$  is an analytic function of  $z$  for  $R(z) \geq 0$  and is of order  $(\rho, k)$ ,  $0 \leq k < \pi$ , and where  $a$  and  $b$  are constants such that  $R(a)$  and  $R(b)$  both  $\geq 0$ . Then  $f_1(s)$  and  $f_2(s)$  have the same line of absolute convergence, and the same singularities.

$$\sum_{\nu=1}^{\nu=n} \phi(a+\nu) e^{-s(a+\nu)} = \frac{1}{2\pi i} \int_O \frac{\phi(a+z) e^{-s(a+z)}}{e^{2\pi iz} - 1} dz,$$

where  $O$  is the contour made of the line  $R(z) = \frac{1}{2}$  and the arc of the circle  $|z| = n + \frac{1}{2}$  lying to the right of the line  $R(z) = \frac{1}{2}$ .

By means of the above formula we can easily prove that for certain values of  $s$

$$\begin{aligned} \sum_1^{\infty} \phi(a+\nu) e^{-s(a+\nu)} &= e^{-as} \int_{\frac{1}{2}}^{\frac{1}{2}-i\infty} \frac{\phi(a+z) e^{-sz}}{e^{2\pi iz} - 1} dz - e^{-as} \int_{\frac{1}{2}}^{\frac{1}{2}+i\infty} \frac{\phi(a+z) e^{-sz}}{e^{2\pi iz} - 1} dz \\ &= e^{-as} \int_{\frac{1}{2}}^{\infty} \phi(a+z) e^{-sz} dz \\ &\quad + e^{-as} \int_{\frac{1}{2}}^{\frac{1}{2}+i\infty} \frac{\phi(a+z) e^{-sz}}{e^{-2\pi iz} - 1} dz + e^{-as} \int_{\frac{1}{2}}^{\frac{1}{2}-i\infty} \frac{\phi(a+z) e^{-sz}}{e^{2\pi iz} - 1} dz \end{aligned}$$

Now, it is easy to see that the second integral is absolutely and uniformly convergent over the region  $2\pi - k \geq t + \delta > t$ ,  $\sigma$  bounded, and that the third integral over the region

$$t \geq -(2\pi - k) + \delta > -(2\pi - k).$$

Hence, both the integrals represent an analytic function of  $s$  in any finite part of the strip  $|t| \leq \pi$ .

Thus, by the principle of analytic continuation

$$e^{-as} f_1(s) = e^{-as} \sum_0^{\infty} \phi(a+n) e^{-sn} = g_1(s) + e^{-as} \int_0^{\infty} \phi(a+z) e^{-sz} dz,$$

$$\text{and } e^{-bs} f_2(s) = e^{-bs} \sum_0^{\infty} \phi(b+n) e^{-sn} = g_2(s) + e^{-bs} \int_0^{\infty} \phi(b+z) e^{-sz} dz,$$

where  $g_1(s)$  and  $g_2(s)$  are analytic functions of  $s$  in any finite part of the strip  $|t| \leq \pi$ .

Now the proposition follows by an application of the preceding result (b). This gives an extension of another result due to Polya.<sup>5</sup>

(d) Theorem IV enables us to study the singularities of the Dirichlet's series

$$\sum_1^{\infty} \phi(\log n) n^{-s+1}. \text{ Proceeding as in (c) above it can be established that}$$

$$\sum_1^{\infty} \phi(\log n) n^{-s+1} = G(s) + \int_0^{\infty} \phi(z) e^{-sz} dz,$$

where  $G(s)$  is an integral function of  $s$ .

Thus the singularities of the Dirichlet's series and the integral  $\int_0^{\infty} \phi(z) e^{-sz} dz$  are identical.

(e) If  $\phi(z)$  is an analytic function of  $z$  in the half-plane  $R(z) \geq 0$  and is of order  $e^{\kappa\rho}$ ,  $0 \leq \kappa < \pi$ , then

$$\overline{\lim}_{n \rightarrow \infty} |\phi(n)|^{\frac{1}{n}} = \overline{\lim}_{\rho \rightarrow \infty} |\phi(\rho)|^{\frac{1}{\rho}},$$

where  $n$  has the integral values 1, 2, 3, 4... and  $\rho$  passes through all the positive values.

$$\text{Let } \overline{\lim}_{n \rightarrow \infty} |\phi(n)|^{\frac{1}{n}} = e^{\alpha} \text{ and } \overline{\lim}_{\rho \rightarrow \infty} |\phi(\rho)|^{\frac{1}{\rho}} = e^{\lambda(0)}.$$

Now, let us consider  $F(s)$  defined by

$$F(s) = \sum_0^{\infty} \phi(v) e^{-sv}.$$

By a well-known formula this power series in  $e^{-s}$  has  $\sigma = \alpha$  for its line of absolute convergence, and on this line at least one singularity of  $F(s)$  lies.

Also, proceeding as in (c), we get the relation

$$\begin{aligned} F(s) &= g(s) + \int_0^{\infty} \phi(z) e^{-sz} dz \\ &= g(s) + f(s), \end{aligned}$$

where  $g(s)$  is an analytic function of  $s$  in any finite part of the strip  $|t| \leq \pi$ , and  $f(s)$  is analytic outside a convex curve  $\Sigma$ , which on account of the restriction on  $k$  lies entirely in the strip  $|t| \leq \pi$ . That is, all the finite singularities of  $F(s)$  in the strip  $|t| \leq \pi$  are identical with those of  $f(s)$ .

Now by virtue of theorem IV, the line of absolute convergence of the integral  $\int_0^{\infty} \phi(z) e^{-sz} dz$ , viz.  $\sigma = \lambda(0)$ , has at least one singularity of  $f(s)$  lying on it, and  $f(s)$  is analytic to the right of this line. Hence the lines  $\sigma = \lambda(0)$  and  $\sigma = \alpha$  are identical, that is  $\alpha = \lambda(0)$ .

This proposition is a generalization of another result due to Polya.<sup>6</sup>

#### References.

- <sup>1</sup> G. Polya, *Math. Zeitschrift*, 92, 606, 1928.
- <sup>2</sup> C. Jourdan, *Cours d'Analyse*, 3rd edition, Vol. 2, p. 277, 1913.
- <sup>3</sup> Hardy, *Acta Math.*, 42, 333.
- <sup>4</sup> G. Polya, *Math. Zeitschrift*, 29, 590, 1929.
- <sup>5</sup> *Loc. cit.*, p. 608.
- <sup>6</sup> *Loc. cit.*, p. 606.

## SOME NEW ULTRA-VIOLET SOLUTION LIGHT FILTERS.

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It is highly essential in photochemical reactions to have a monochromatic source of light to study the effect of various wavelengths. We have already investigated some of the light filters and their visible transmissions.<sup>1</sup> In this paper the use of certain solutions for the transmission of purely ultraviolet radiations is very briefly discussed.

It is well known that the addition of nickel oxide makes a glass very suitable for the transmission of ultraviolet rays and cuts off visible and infra-red radiations.<sup>2</sup> Nickel chloride, nickel nitrate, nickel sulphate  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$  and nickel acetate have been examined<sup>3</sup> in search of a substance for the complete absorption of infra-red radiations. No quantitative investigations seem to have been made concerning the visible and ultraviolet transmission of these salts. Moreover, the variation in absorption with change in concentration is unknown. I have studied nickel nitrate singly, as well as in combination with potassium dichromate, picric acid and cobalt chloride, from all these considerations. Some of my results are recorded below.

Experimental arrangement for the determination of absorption was the same as described in previous papers. For visible, point-o-light and Nutting's spectrophotometer and for ultraviolet copper arc and quartz spectrograph were used. The results are given in the following tables where  $\lambda$  = wavelength in Å units; T = transmission;  $l$  = thickness of the solution in quartz cell;  $d$  = density reading and  $e$  = extinction coefficient.

## Measurements in the Visible

Table 1.—Ni (NO<sub>3</sub>)<sub>2</sub>. 4.16M.  $l=1$  cm.

| $\lambda$ | $d$      | % T   | $\lambda$ | $d$      | % T  |
|-----------|----------|-------|-----------|----------|------|
| 4400      | $\infty$ | 0     | 5200      | 1.17     | 6.7  |
| 4500      | 3.20     | 0.063 | 5600      | 1.25     | 5.6  |
| 4600      | 2.45     | 0.35  | 5800      | 1.95     | 1.1  |
| 4800      | 1.30     | 5.0   | 5900      | 2.65     | 0.22 |
| 5000      | 1.10     | 7.9   | 6100      | $\infty$ | 0    |

Table 2.—Ni (NO<sub>3</sub>)<sub>2</sub>. 2.08M.  $l=1$  cm.

| $\lambda$ | $d$  | % T  | $\lambda$ | $d$      | % T   |
|-----------|------|------|-----------|----------|-------|
| 4300      |      | 0    | 5600      | 0.60     | 25.1  |
| 4600      | 1.20 | 6.3  | 5800      | 0.96     | 10.9  |
| 4800      | 0.57 | 26.9 | 6200      | 3.0      | 0.1   |
| 5000      | 0.52 | 30.2 | 6300      | 3.8      | 0.016 |
| 5200      | 0.55 | 28.1 | 6400      | $\infty$ | 0     |

Table 3.—Ni (NO<sub>3</sub>)<sub>2</sub>. 1.04M.  $l=1$  cm.

| $\lambda$ | $d$  | % T  | $\lambda$ | $d$  | % T  |
|-----------|------|------|-----------|------|------|
| 4400      | 0.82 | 15.1 | 5800      | 0.47 | 33.8 |
| 4800      | 0.30 | 50   | 6000      | 0.83 | 14.7 |
| 5000      | 0.25 | 56.2 | 6400      | 1.90 | 1.26 |
| 5400      | 0.27 | 53.7 | 7000      | 2.45 | 0.35 |

Table 4.—Ni (NO<sub>3</sub>)<sub>2</sub> 0.208M.  $l=1$  cm.

| $\lambda$ | $d$  | % T  | $\lambda$ | $d$   | % T  |
|-----------|------|------|-----------|-------|------|
| 4400      | 0.16 | 69.1 | 5800      | 0.09  | 81.5 |
| 4800      | 0.06 | 87.1 | 6000      | 0.016 | 69.2 |
| 5000      | 0.04 | 91.2 | 6400      | 0.36  | 43.6 |
| 5200      | 0.05 | 89.1 | 7000      | 0.45  | 35.5 |

Table 5.—K<sub>2</sub> Cr<sub>2</sub> O<sub>7</sub> 0.513M.  $l=1$  cm.

| $\lambda$ | $d$      | % T  | $\lambda$ | $d$  | % T  |
|-----------|----------|------|-----------|------|------|
| 5350      | $\infty$ | 0    | 5700      | 0.20 | 63.0 |
| 5400      | 2.8      | 0.16 | 5800      | 0.14 | 72.4 |
| 5500      | 1.06     | 8.7  | 5900      | 0.04 | 91.2 |
| 5600      | 0.40     | 39.8 | 6000      | 0.04 | 91.2 |

Table 6.—K<sub>2</sub> Cr<sub>2</sub> O<sub>7</sub> 0.256M.  $l=1$  cm.

| $\lambda$ | $d$      | % T   | $\lambda$ | $d$  | % T  |
|-----------|----------|-------|-----------|------|------|
| 5200      | $\infty$ | 0     | 5500      | 0.52 | 30.2 |
| 5300      | 3.40     | 0.039 | 5600      | 0.20 | 63.0 |
| 5400      | 1.32     | 4.78  | 5800      | 0.02 | 95.5 |

Table 7.—K<sub>2</sub> Cr<sub>2</sub> O<sub>7</sub> 0.0513M.  $l=1$  cm.

| $\lambda$ | $d$      | % T  | $\lambda$ | $d$  | % T  |
|-----------|----------|------|-----------|------|------|
| 5000      | $\infty$ | 0    | 5500      | 0.10 | 79.4 |
| 5100      | 2.76     | 0.17 | 5800      | 0.04 | 91.2 |
| 5200      | 1.40     | 3.9  | 6000      | 0.02 | 95.5 |
| 5400      | 0.25     | 56.2 | 6200      | ...  | ...  |

Table 8.—CoCl<sub>2</sub> 3.66 M.  $l=1$  cm.

| $\lambda$          | $d$      | %T   | $\lambda$ | $d$  | %T   |
|--------------------|----------|------|-----------|------|------|
| 4000<br>to<br>7100 | $\infty$ | 0    | 7300      | 1.60 | 2.5  |
| 7200               | $\infty$ | 0    | 7400      | 1.20 | 6.3  |
|                    | 3.01     | 0.01 | 7600      | 0.95 | 11.2 |

Table 9.—CoCl<sub>2</sub> 1.83 M.  $l=1$  cm.

| $\lambda$          | $d$      | %T    | $\lambda$ | $d$  | %T   |
|--------------------|----------|-------|-----------|------|------|
| 4300               | 2.25     | 0.56  | 5800      | 1.70 | 1.9  |
| 4400               | 3.75     | 0.017 | 6000      | 1.05 | 8.9  |
| 4500<br>to<br>5500 | $\infty$ | 0     | 6200      | 0.85 | 14.1 |
|                    | $\infty$ | 0     | 6600      | 0.82 | 15.1 |
| 5700               | 2.65     | 0.22  | 7200      | 0.50 | 31.6 |

Table 10.—CoCl<sub>2</sub> 0.915 M.  $l=1$  cm.

| $\lambda$          | $d$      | %T   | $\lambda$ | $d$  | %T    |
|--------------------|----------|------|-----------|------|-------|
| 4200               | 0.93     | 11.7 | 5400      | 3.75 | 0.017 |
| 4400               | 1.6      | 2.5  | 5800      | 0.73 | 18.6  |
| 4600               | 3.15     | 0.07 | 6200      | 0.46 | 34.6  |
| 4900<br>to<br>5200 | $\infty$ | 0    | 6400      | 0.42 | 38.0  |
|                    | $\infty$ | 0    | 7000      | 0.32 | 47.8  |

Table 11.—CoCl<sub>2</sub> 0.183 M.  $l=1$  cm.

| $\lambda$ | $d$  | %T   | $\lambda$ | $d$  | %T   |
|-----------|------|------|-----------|------|------|
| 4200      | 0.25 | 56.0 | 5600      | 0.28 | 52.4 |
| 4400      | 0.35 | 44.6 | 5800      | 0.10 | 79.4 |
| 4600      | 0.59 | 25.7 | 6000      | 0.08 | 83.1 |
| 4800      | 0.69 | 20.4 | 6600      | 0.07 | 85.1 |
| 5400      | 0.55 | 28.1 | 7000      | 0.05 | 89.1 |



*Table 12.*—Ni (NO<sub>3</sub>)<sub>2</sub> 4·16 M + K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> 0·513M. each in one centimeter cell.

| $\lambda$ | $d$      | %T   | $\lambda$ | $d$      | %T    |
|-----------|----------|------|-----------|----------|-------|
| 5400      | $\infty$ | 0    | 5800      | 2·10     | 0·79  |
| 5500      | 2·30     | 0·50 | 5900      | 2·70     | 0·20  |
| 5600      | 1·70     | 1·99 | 6000      | 4·5      | 0·003 |
| 5700      | 1·70     | 1·99 | 6100      | $\infty$ | 0     |

*Table 13.*—Ni (NO<sub>3</sub>)<sub>2</sub> 4·16 M + K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> 0·256 M each in 1 cm. cell.

| $\lambda$ | $d$      | %T   | $\lambda$ | $d$      | %T    |
|-----------|----------|------|-----------|----------|-------|
| 5300      | $\infty$ | 0    | 5800      | 2·0      | 1·0   |
| 5400      | 2·60     | 0·25 | 5900      | 2·65     | 0·22  |
| 5500      | 1·75     | 1·7  | 6000      | 4·5      | 0·003 |
| 5600      | 1·45     | 3·5  | 6100      | $\infty$ | 0     |

*Table 14.*—CoCl<sub>2</sub> 3·66 M + K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> of any concentration each in 1 cm. cell.Transmits same as CoCl<sub>2</sub> 3·66M.*Table 15.*—CoCl<sub>2</sub> 1·83 M + K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> 0·513 M. each in 1 cm. cell.

| $\lambda$ | $d$      | %T   | $\lambda$ | $d$  | %T   |
|-----------|----------|------|-----------|------|------|
| 5500      | $\infty$ | 0    | 6000      | 1·10 | 7·9  |
| 5700      | 2·85     | 0·14 | 9200      | 0·85 | 14·0 |
| 5800      | 1·84     | 1·4  | 7200      | 0·50 | 31·6 |

*Table 16.*—Ni (NO<sub>3</sub>)<sub>2</sub> 2·08 M + K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> 0·513 M. each in 1 cm. cell.

| $\lambda$ | $d$      | %T    | $\lambda$ | $d$      | %T     |
|-----------|----------|-------|-----------|----------|--------|
| 5350      | $\infty$ | 0     | 6000      | 1·70     | 1·99   |
| 5400      | 3·40     | 0·025 | 6200      | 3·0      | 0·10   |
| 5600      | 1·70     | 1·99  | 6300      | 3·7      | 0·0199 |
| 5800      | 1·05     | 8·9   | 6400      | $\infty$ | 0      |

*Table 17.*— $\text{Ni}(\text{NO}_3)_2$  4.16 M +  $\text{CoCl}_2$  3.66 M. each in 1 cm. cell.  
Transmits no visible.

*Table 18.*— $\text{Ni}(\text{NO}_3)_2$  2.08 M +  $\text{CoCl}_2$  3.66 M. each in 1 cm. cell.  
Transmits no visible.

| 19 $\text{Ni}(\text{NO}_3)_2$ 4.16 M + $\text{CoCl}_2$ 1.83 M. each in 1 cm. cell. |          |        | 20 $\text{Ni}(\text{NO}_3)_2$ 2.08 M + $\text{CoCl}_2$ 1.83 M. each in 1 cm. cell. |          |       |
|--|----------|--------|--|----------|-------|
| $\lambda$  | $d$      | %T     | $\lambda$  | $d$      | %T    |
| 5606   | $\infty$ | 0      | 5600   | $\infty$ | 0     |
| 5700   | 4.4      | 0.0025 | 5800   | 2.70     | 0.2   |
| 5800   | 3.70     | 0.02   | 6000   | 2.75     | 0.17  |
| 5900   | 4.0      | 0.01   | 6200   | 3.90     | 0.012 |
| 6000   | $\infty$ | 0      | 6300   | $\infty$ | 0     |

#### Infra-red Transmission (4)

*Table 1.*— $\text{Ni}(\text{NO}_3)_2$ . 10 gms. in 100 c. cs. of water  $l=1\text{cm}$ .

| $\lambda$ | % T | $\lambda$ | % T |
|-----------|-----|-----------|-----|
| 6000      | 42  | 10000     | 33  |
| 7000      | 11  | 11000     | 15  |
| 8000      | 50  | 12000     | 8   |
| 9000      | 64  | 13000     | 4   |

*Table 2.*— $\text{Ni}(\text{NO}_3)_2$ . (a) 4.16 M. (b) 2.08 M.  $l=1\text{cm}$ .

calculated from (1) assuming Beer's law absorption.

| $\lambda$ | % T (a) | % T (b) | $\lambda$ | % T (a) | % T (b) |
|-----------|---------|---------|-----------|---------|---------|
| 6000      | 0.29    | 5.4     | 10000     | 0.037   | 1.99    |
| 7000      | 0       | 0.04    | 11000     | 0       | 0.12    |
| 8000      | 0.67    | 8.3     | 12000     | 0       | 0.026   |
| 9000      | 3.98    | 10.2    | 13000     | 0       | 0       |

## Ultra-violet and Visible Transmission (photographically)

| Salt   | Time of exposure | Visible     | Ultra-violet               |
|--|------------------|-------------|----------------------------|
| (1) $K_2Cr_2O_7$ any concentration $>0.005$ M. ... | 4 hours.         | —           | Nil                        |
| (2) $Ni(NO_3)_2$ 4.16 M. ...                       | 5 "              | 4415—6100A° | 3327—3527A°                |
| (3) $Ni(NO_3)_2$ 2.08 M. ...                       | 2 "              | 4300—6400A° | 3307—3598A°                |
| (4) $Ni(NO_3)_2$ 2.08M + $CoCl_2$ 1.83 M. ...      | 4 "              | 5600—6300A° | 3307—3598A°                |
| (5) $Ni(NO_3)_2$ 4.16 M + $CoCl_2$ 3.66 M. ...     | 4 "              | Nil         | 3420—3527 (Faint)          |
| (6) $Ni(NO_3)_2$ 4.16M + $CoCl_2$ 1.83 M. ...      | 4 "              | 5600—6000A° | 3337—3527A°                |
| (7) Corning violet-ultra ...                       | 4 "              | Nil         | 3248—3825A°                |
| (8) $Ni(NO_3)_2$ 2.08 M + $CoCl_2$ 3.66 M. ...     | ...              | Nil         | 3307—3598A°                |
| (9) $CoCl_2$ 3.66M. ...                            | 4 "              | 7100—7600A° | 2618—4063A°                |
| (10) $CoCl_2$ 3.66 M + $K_2Cr_2O_7$ 0.00154 M. ... | 5 "              | 7100—7600A° | 4023—4063 and 3290—2961 A° |

It will be observed that the filters Nos. 5 to 10 are suitable for ultraviolet transmission. The intensity of filter No. 5 is extremely low. Filter No. 6, although it transmits little of visible in addition to the same ultraviolet as filter No. 8 its transmission is practically the same. Corning violet is comparable with filter No. 8 the ultraviolet range being much smaller than the corning filter. Filter No. 9 transmits highly in the ultraviolet in addition to far in the red. (7100—7600)°. So far photochemical reactions are concerned this transmission on the longer wavelength side has got practically no effect and hence the filter is useful for ultraviolet work.

A. K. Bhattacharya has used my filters and determined the velocity of the photochemical decomposition of ferric thiocyanate and studied the reaction between potassium oxalate and bromine, using quartz mercury vapour lamp as light source. His results of the velocity constants are recorded below.

|  | Ferrithiocyanate<br>$K_1$ | Potassium oxalate<br>and bromine. $K_1$ |
|--|---------------------------|---|
| (7) Corning glass. ultraviolet ...           | 0.000987.                 | 0.0139                                  |
| (8) $Ni(NO_3)_2$ 2.08M + $CoCl_2$ 3.66 M ... | 0.00107                   | 0.0137                                  |
| (9) $CoCl_2$ 3.66M ...                       | 0.00176                   | 0.0183                                  |

These results clearly show that the filter No. 9 is decidedly superior to filter Nos. 7 and 8, both of which are equally good. In view of the fact the range of transmission of filter No. 8 is much shorter than the corning glass the filter is

therefore decidedly better than No. 7. I therefore recommend my following two solution light filters for ultraviolet work.

|                                    |     |     | Transmits                      |
|------------------------------------|-----|-----|--------------------------------|
| Filter (8) Cobalt chloride 3'66 M. | ... | ... | 3307—3598 Å                    |
| Nickel nitrate 2'08 M.             | ... | ... |                                |
| Filter (9) Cobalt chloride 3'66 M. | ... | ... | 2618—4063 Å and<br>7100—7600 Å |

The filter No. 10 is also very useful as it transmits lower ultraviolet, the range at the same time being much shorter than cobalt chloride alone. This filter has not been worked out as yet and the further work is in progress.

In the conclusion I wish to express my indebtedness to Prof. N. R. Dhar for his constant guidance and help in the course of this work. My thanks are also due to A. K. Bhattacharya for allowing me to use his results.

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# AGEING OF HYDROSOLS OF FERRIC PHOSPHATE AND VANADIUM PENTOXIDE

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In the course of the study of viscosity of ferric phosphate sol at various pressures the authors observed<sup>1</sup> that a fairly pure sample of ferric phosphate when heated sets to a firm jelly and again passed into the sol condition when cooled. This behaviour was also observed with other sols like those of  $\text{Al}(\text{OH})_3$ , prepared by hydrolysing aluminium acetate and ferric arsenate. This observation appears interesting and in order to throw light on the mechanism of such change the viscosity, electrical conductivity and the stability of ferric phosphate sol at various temperatures were measured.

Ferric phosphate sol was obtained by the interaction of  $\text{FeCl}_3$  and  $\text{KH}_2\text{PO}_4$  and the sol thus prepared was allowed to dialyse for five days to free it from chloride ions. It was not possible to free the sol completely from the chloride ions because the sol at this stage becomes very viscous and finally sets to a firm jelly. The sol thus prepared was of a deep red colour and contained 32.1 grams of ferric phosphate and 0.4328 grams of chlorine ion per litre of the sol.

Our results on the measurement of the viscosity of the sol at temperatures  $30^\circ$ ,  $40^\circ$ ,  $50^\circ$  and  $60^\circ\text{C}$  show that the viscosity first decreases and then increases remarkably with increasing temperature. The electrical conductivity continuously increases, the percentage of increase or the temperature coefficient of the electrical conductivity is greater than that for an electrolyte at these temperatures. The stability of the sol and the ratio of the precipitating concentration of  $\text{KCl}$  to that of  $\text{BaCl}_2$  rapidly diminishes showing that the electric charge on the colloid particles decreases.<sup>2</sup>

It was found that the sol very quickly shows a change in the properties studied in this paper at the higher temperatures with time. We have, therefore, investigated the changes in these properties at the temperatures  $40^\circ$ ,  $50^\circ$  and  $60^\circ\text{C}$  with time.

Our experimental results show that within 6 hours of observation the changes were more pronounced at higher temperatures than at lower ones. At  $40^\circ$ ,  $50^\circ$  and  $60^\circ\text{C}$  both the viscosity and the electrical conductivity continue to increase and the stability and the ratio of the precipitating concentration of  $\text{KCl}$  to  $\text{BaCl}_2$  are slightly decreased. At  $60^\circ\text{C}$  the changes in the viscosity of the sol was so rapid that it sets to a firm gel after five hours.

After keeping the sol at the higher temperature for six hours it was brought to a bath maintained at  $20^{\circ}\text{C}$  and the viscosity, electrical conductivity and the stability towards  $\text{KCl}$  and  $\text{BaCl}_2$  were measured for 48 hours. It was found that the sols treated at higher temperatures showed greater viscosity and electrical conductivity and was less stable than the sol kept at ordinary room temperature and this was more in magnitude for the sols treated at a higher temperature than that at a lower one. As the sols were kept at  $20^{\circ}\text{C}$ , the viscosity and the electrical conductivity diminished and the stability and the electric charge on the colloid particles appreciably increased with time tending to reach the condition of the sol which is kept only at the room temperature. It was found that the viscosity and the electrical conductivity were greater and the stability (and hence the electric charge) remained less than the sol kept at the room temperature even after keeping the sols at  $20^{\circ}\text{C}$  for five days. When these viscous sols were highly agitated by shaking, their viscosities decreased appreciably but there was no change in their electrical conductivities and in their stability.

These results obtained with a sol of ferric phosphate which is positively charged, show that at higher temperatures the adsorbed electrolyte that stabilises the sol is given out gradually making the sol less stable, more conducting and more viscous. It is apparent that this behaviour is expected to be more marked at higher temperatures than at lower ones. When these sols, rendered more viscous and electrically conducting and less stable at a higher temperature, are brought to a lower temperature, the electrolyte given out at higher temperature, is again taken up gradually by the colloid particles making the sol less viscous and conducting and more stable with time. As the colloid kept at a higher temperature ages and hence loses the adsorptive capacity more quickly than that kept at the room temperature, it is easy to see that for the former sols the viscosity, conductivity and the electric charge on colloid particles cannot reach the values as those for the latter one.

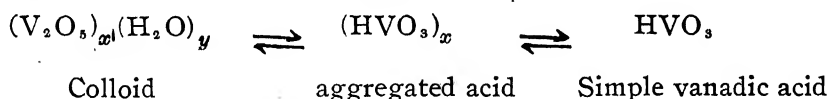
It is generally believed by the colloid chemists that a highly viscous sol is essentially connected with the high hydration of colloid particles. We have, therefore, to conclude from this that the colloid particles of ferric phosphate becomes more hydrated at higher temperatures, so much so that 3.2 per cent of  $\text{FePO}_4$  is associated with the rest of the water of the sol and the sol is converted into a gel at  $60^{\circ}\text{C}$ . It is, however, not possible to understand how a colloid particle, which loses its adsorptive capacity at higher temperatures is hydrated to a greater extent than a colloid particle which has high adsorptive power and is less hydrated at a lower temperature. We are, therefore, of opinion as we have expressed in our previous communication<sup>1</sup> that in the case of so-called highly viscous sols all that we measure is the structural flow and not the true viscosity. As the ferric phosphate colloid particle loses the stabilising electrolyte, the electrical charge is decreased and the chances for the formation of a structure in the sol is increased. This structure is formed as we have already pointed out in our publications in this

subject from a 'loose crystallographic force.' Our views are further strengthened by our observation that a sol of ferric phosphate kept at a temperature of  $50^\circ C$  becomes more rapidly viscous when the sol is sewn with an already formed gel of ferric phosphate of the same concentration as the sol. This sowing does not effect the electrical conductivity and the stability. That this structure is maintained even when the sol is brought to a lower temperature can be shown by the fact that the viscosity can be appreciably diminished by agitating the sol by shaking and the phenomenon is alike to that observed by us during the course of gelation of sols of agar and gelatin read before the academy and nomenclatured as 'hysteresis in the process of gelation.'<sup>3</sup>

Our results on the ferric phosphate sol lead to another important issue, *viz.*, the effect of time on this sol is dependent on the previous treatment that the sol has undergone. Thus the sol prepared at lower temperatures when brought to a higher one it shows an increase in viscosity and the electrical conductivity and a decrease in stability, whilst the very sol shows a different behaviour when brought from a higher temperature to a lower one.

It may be of interest that D. N. Chakravarti\* has studied the influence of time for over three months on the viscosity and the electrical conductivity of ferric phosphate sol at ordinary temperature of the room. These results show that the viscosity decreases and the electrical conductivity increases with time. We are of opinion that in view of the fact that the greater time was allowed by this investigator in the ageing of the sol, sufficient aggregation of the colloid particles occurred with the consequent decrease in the viscosity and increase in the electrical conductivity.

We shall now report an abstract of our results obtained with vanadium pentoxide sol on the similar experimental lines as followed in the case of ferric phosphate sol. This sol required investigation as it has been proved by one of the authors of this paper in collaboration with Professor N. R. Dhar<sup>†</sup> that it belonged to a separate class of colloids because it contains some of the substance in the molecular condition according to the scheme



Vanadium pentoxide sol was prepared by precipitating vanadic acid from ammonium vanadate by the action of concentrated HCl and then washing the precipitate till it has a tendency to pass to a colloidal state. The whole of the precipitate is now shaken with distilled water and the sol thus formed is allowed to dialyse till it was free from HCl.

It was found that the viscosities of vanadium pentoxide sol diminish more rapidly than those of water on increasing the temperature. The electrical conductivity also increased remarkably. Though the amounts of KCl and BaCl<sub>2</sub> necessary to

coagulate the sol diminished but the ratio of their precipitating concentrations increased with the increasing temperature showing an increase in the electric charge on the colloid particles.

Influence of time on the viscosity, electrical conductivity and stability of vanadium pentoxide sol at 40°, 50° and 60° C were also measured and it was found that in all cases the viscosity diminishes and the electrical conductivity and the electrical charge on the colloid particles gradually increase, the effect being more pronounced at higher temperatures than that at a lower one. This is most probably due to the fact that more of molecular vanadic acid is formed at the expense of the colloidal aggregates of the sol and this therefore makes the sol less viscous, more conducting and more stable.

It must be recalled here that silicic acid sol which belongs to the same class of colloids as that of vanadium pentoxide rapidly increases in viscosity and finally sets to a firm gel when heated.

It will be of interest to note in this paper that a diminution of the electric charge on a colloid particle increases the viscosity of a sol and *vice versa* and it is in agreement with the conclusion of Dhar.<sup>6</sup> Smoluchowski,<sup>7</sup> on the other hand, concludes that the viscosity of a sol should increase with the increasing charge on the colloidal particle.

We are of opinion that the rate of flow of a sol under a definite pressure should diminish as the electric charge on a colloid particle decreases. We have shown elsewhere that in the flow for the so-called highly viscous sols the simple rule of viscosity, *viz.*, rate of flow is directly proportional to the pressure causing the flow, is not applicable. We have concluded in the same paper that some kind of structure is formed amongst the colloid particles. Smoluchowski has not taken this into account and hence his conclusion has no experimental support. Again the effect of the variation in the hydration of the colloid particles due to a change in the electrical charge on the colloid particles may change the total effective volume of the colloid more prominently and thence the viscosity than the electro-viscous effect of Smoluchowski.

In conclusion the authors desire to express their indebtedness to Professor N. R. Dhar in giving his valuable suggestions in the progress of this work.

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# CHEMICAL EXAMINATION OF THE SEEDS OF THEVETIA NERIIFOLIA (JUSS), PART I.

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*Thevetia neriifolia* (N. O. Apocynaceæ) or yellow oleander as it is known in English, *pila-kaner* in Hindustani and *kalki-phul* in Bengali is a common garden plant in India generally cultivated for its bright yellow ornamental flowers and clusters of long deep pointed leaves. The plant scarcely attains a height of more than fifteen feet and is covered with a smooth greenish grey bark which, when cut or broken, yields a copious milky secretion. The fruit has got the external appearance of a pyramid on a hemispherical base and is often nearly two inches in length, but after the fleshy portion is removed it yields a hard brown triangular nut, with a deep groove or cleft in the middle along which the nut can be easily broken to yield two complete pieces of white flattened kernels covered with a thin onion coloured membrane. The kernels are extremely bitter.

The whole plant is poisonous, particularly so is the fruit, which has been responsible for many suicides in Bengal and many cases of cattle poisoning in the Bombay Presidency. On account of its poisonous nature, *i.e.*, to say its intense physiological reactivity, various parts of the plant have from time to time been used as remedies for various ailments, *e.g.*, the bark as an emetic and antiperiodic and in larger doses drastic purgative; the juice as vesicant; the fruit as a powerful emetic; the root as an antipyretic and so on. For detailed information reference may be made to Dymock's *Pharmacographia Indica*, Vol. 2, pp. 406—410. The seeds

contain an active principle which has been isolated in the crude form by various authors and has been found to be a strong cardiac poison producing death in large doses by asphyxia and paralysis of the heart with great lowering of the body temperature. It is a strong irritant for the skin, producing a mass of minute eruptions resembling eczema. In ordinary doses it produces convulsions.

De Vrij<sup>1</sup> discovered in the seeds a glucoside (which apparently he could not obtain in a pure form since no melting point or formula is given), which was closely studied by Blas. Blas and Husemann<sup>2</sup> tested the action of the glucoside on animal and found it to have the same effect on frogs as digitalin. Apart from the isolation of thevetin, referred to above, De Vrij also found that the kernels of the seeds give with benzine 57 per cent of a limpid oil. Bhattacharya and Ayyar<sup>3</sup> also obtained with light petroleum a yellow oil, the oil content being 57 per cent. In addition to thevetin the existence of a second poisonous principle in the seed was proved by Warden,<sup>4</sup> who isolated an amorphous sticky resin from the mother liquor from which thevetin had been extracted. Warden also extracted a blue principle from the seeds of *Thevetia neriifolia* in the form of a dark amorphous insoluble powder by the action of concentrated hydrochloric acid on the purified aqueous extracts of the oil free kernels. This blue substance which he named 'thevetin-blue,' was thought by the author to be pseudo-indican.

Blas<sup>5</sup> gave the formula  $C_{54}H_{84}O_{24} + 3 H_2O$  to thevetin, m. p.  $170^{\circ}C$ , the active principle and  $C_{48}H_{70}O_{10} + 2 H_2O$  to the aglucone, which he named theveresin, m. p.,  $140^{\circ}C$ .

R. Weitz and A. Boulay<sup>6</sup> also extracted a bitter principle from the kernels which gave with  $H_2SO_4$  an orange-yellow coloration, becoming pink after 12 hours.

The above represents the work that has hitherto been recorded in chemical literature on the kernels of the fruit of *Thevetia neriifolia*. A systematic analysis of the kernels of the seed was therefore undertaken with a view to study the exact chemical nature of the poisonous ingredients contained in it. 68.7 per cent of a non-drying light yellow oil and two crystalline glucosides have been isolated from the kernels of the seeds.

#### EXPERIMENTAL

Full-grown fruits of *Thevetia neriifolia* were collected during the months of October and November. After keeping the fruits for about a week the outer green fleshy portion got blackened and were easily removed when the hard nuts were obtained. The nuts contained 22.6 per cent of kernels. The kernels were covered with a light brown coating which constituted 6.4 per cent of it. On estimation, the kernels were found to contain 23 per cent of moisture.

Fifty grammes of the crushed kernels were freed from oil by cold petroleum ether extraction. The oil free powder was put in a flask with 200 c. c. distilled water and few drops of chloroform at room temperature for three days. The

filtrate gave a white flaky precipitate on addition of absolute alcohol. The precipitate was washed with alcohol and added to aqueous-alcoholic solution of hydroquinone kept at 30°C. The solution was slowly coloured green with the formation of quinhydrone, showing thereby the presence of an oxidising enzyme in the precipitate.

Twenty grammes of the oil-free kernels were tested for the presence of alkaloids, but with negative result.

After completely burning the kernels 1.9 per cent of white residue (ash) was obtained, which contained 3.1 per cent of  $\text{SiO}_2$ . The soluble portion of the ash contained phosphate, chloride, nitrate (traces) and magnesium.

The light brown coating of the kernels were carefully separated and 50 g. of it was extracted with ethyl alcohol. The extract was yellowish green in colour. The alcohol was distilled off till about 15 c.c. were left and was kept overnight. Next morning ill-defined soft crystalline mass was found settled at the bottom, which on examination was found to be a mixture of wax and chlorophyll.

For complete analysis 1.5 kilograms of the air dried and crushed kernels were exhaustively extracted with five liters of petroleum ether (b.p. 35–60°C.) in a round bottom extraction flask, till a portion of the extract no longer gave any oily residue on evaporation. The total quantity of the oil obtained amounted to 1,030 g., which corresponded to 68.7 per cent of the kernels. It was a non-drying oil and on purification with Fuller's earth and animal charcoal became very light yellow in colour. It had a sweet bland taste and was entirely free from poisonous properties. In fact its chemical and physical properties corresponded very closely to those of olive oil and in the opinion of the author should form an excellent economic proposition as an article of food and toilet specially in view of the large yield. The oil was not further examined in view of the work already done by Bhattacharya and Ayyar.<sup>3</sup>

The oil-free kernels were completely freed from petroleum ether and successively extracted with rectified spirit till a portion of the extract gave only traces of residue on complete evaporation. The alcoholic extract was concentrated under reduced pressure when a thick brown syrupy liquid, strongly smelling of sugar, was obtained. This slowly solidified to a brown hygroscopic mass in a vacuum desiccator. On extraction with chloroform it gave 40 g. of yellowish brown solid on complete evaporation of the solvent. This substance was completely soluble in ethyl acetate. Traces of oil that was contaminated with it was removed by treatment with petroleum ether. On crystallization from dilute alcohol it was obtained as snow white slender needles melting at 192°C., and having a molecular formula  $\text{C}_{20}\text{H}_{30}\text{O}_6$ . This was probably the substance which was isolated in the crude form by De Vrij<sup>1</sup> and named by him as thevetin. This substance is insoluble in water but easily soluble in most of the organic solvents. It does not reduce Fehling's solution or Tollens reagent, but both of them are readily reduced if the compound is previously hydrolysed by warming with concentrated

hydrochloric acid. It does not produce any coloration or precipitate with the usual alkaloid reagents. Alcoholic ferric chloride, lead acetate or sub-acetate, silver nitrate or calcium chloride have no effect on the substance. When perfectly pure the substance is quite tasteless, but in the presence of only traces of impurities it has a pronounced bitter taste. The substance has been named as 'thevetin' by the present author after De Vrij who was the first worker in this field.

The residue left after chloroform extraction was freed from the solvent and dissolved in 400 c.c. water with heating. The liquid which was deep brown in colour was allowed to stand with few drops of chloroform to arrest bacterial growth. After about a week white sediment started separating from the mother liquor and within a fortnight the whole of the vessel was full of a white shining deposit. The product was filtered at the pump and on drying weighed 37 g. This on twice crystallization from hot water was obtained as slender shining silky needles, melting at  $178^{\circ}\text{C}$ . This substance which has the molecular formula  $\text{C}_{16}\text{H}_{24}\text{O}_8$  differs from thevetin by its solubility in water and intense bitter taste. In its chemical deportments, however, it resembles thevetin very closely, giving no reaction with Fehling's, Tollens and alkaloid reagents, and no precipitate with silver nitrate, lead acetate, ferric chloride or calcium chloride. Basic lead acetate, however, produces an abundant flocculent white precipitate on warming. This substance on hydrolysis reduces Fehling's solution and Tollens reagent readily. In working with this substance great care is necessary as the minutest speck of it inhaled as dust produces intense headache and giddiness. On account of highly poisonous character of the substance it has been named as 'thevetoxin.' The physiological examination of the substance, which is still in progress in the King George's Medical College, Lucknow, indicates it to be a strong cardiac poison.

The mother liquor after the separation of thevetoxin was very dark in colour. The volume was made to 500 c.c. and treated with concentrated solution of tannic acid. A black sticky precipitate separated and the colour of the mother liquor became lighter. Excess of tannic acid in the solution was removed by barium hydroxide solution and excess of barium was precipitated by passing carbon dioxide through the solution. The filtrate, which was light green in colour, contained free reducing sugar and a third substance which yielded the greenish-blue colouring matter on treatment with concentrated hydrochloric acid as observed and described by Warden<sup>4</sup> and which probably may contain the pseudo-indican as supposed by him. But up to this time all attempts in the isolation of the product in a pure crystalline form have ended in failure. At best only little yellow amorphous hygroscopic powder has been obtained which has not yielded any constant analytical data. Its purification has been rendered almost impossible on account of its extreme solubility in all the known solvents, and its non-reactivity towards all known precipitating agents.

*Thevetin*,  $C_{20}H_{30}O_6$ .—Thevetin dissolves in concentrated sulphuric acid with the production of yellow colour which slowly changes to pink and finally to cherry-red. Thevetin dissolves in strong nitric acid with a yellow colour. It is optically active having a lævo rotation of  $\left[\alpha\right]_D^{30} = -66.85$  in ethyl alcohol.

[Found: C, 65.40, 65.08, 65.29; H, 8.40, 8.34, 8.22; M. W. (cryoscopic in phenol) 373, 350, 371.  $C_{20}H_{30}O_6$  requires, C, 65.57; H, 8.19; M. W., 366.]

*Hydrolysis of Thevetin*.—3 g. of thevetin was dissolved in 200 c.c. of ethyl alcohol and 150 c.c. of water containing 2.5 c.c. of hydrochloric acid (d. 1.16) was added. It was refluxed for about an hour. The solution was cooled and carefully neutralized with sodium carbonate solution. It was next concentrated under reduced pressure. A semi-solid sticky substance separated. After sufficient of the substance had separated the upper liquid was removed and the product washed several times with water. The aqueous liquid was evaporated to dryness under reduced pressure and the residue dried over calcium chloride in a vacuum desiccator. It was extracted with acetone and the extract evaporated to dryness. It reduced Fehling's solution and copper acetate in dilute acetic acid solution and was proved to be glucose by its phenylosazone, m. p., 205°C. The aglucone—thevetigenin—on purification with alcohol and animal charcoal was obtained in the form of yellowish white soft mass which settled at the bottom. After some time it became brittle, when it was powdered and put in a vacuum desiccator. It melted at 83°C. Strong sulphuric acid produced a pink-red coloration with a green fluorescence. In concentrated nitric acid thevetigenin dissolved with a yellow coloration which intensified on heating. Alcoholic solution of the substance did not give any precipitate or coloration with ferric chloride.

*Thevetoxin*,  $C_{18}H_{24}O_3$ .—Thevetoxin dissolves in strong sulphuric acid with orange coloration which intensifies in about five minutes and becomes deep red. On heating the colour darkens with decomposition of the substance. In strong nitric acid it dissolves with yellow coloration. It is insoluble in most of the organic solvents excepting alcohol, in which it is very soluble. It is sparingly soluble in acetone and moderately soluble in water, from which it crystallizes in slender needles. Thevetoxin is optically active, having a lævo rotation of  $\left[\alpha\right]_D^{30} = -76.1$  in ethyl alcohol. [Found: C, 55.51, 55.60, 54.97; H, 7.33, 7.08, 7.42; M. W. (cryoscopic in phenol) 301, 340, 338.  $C_{18}H_{24}O_3$  requires, C, 55.81; H, 7.00; M. W., 344.]

The hydrolysis of thevetoxin was carried out like that of thevetin. The sugar of hydrolysis was proved to be glucose as in the previous case. The aglucone—thevetoxigenin—on treatment with alcohol and animal charcoal gave a light yellow amorphous powder melting at 81°C. It was soluble in chloroform and dissolved in concentrated sulphuric acid forming an yellow coloration which deepened to red, and on heating, blackened with decomposition. It had a mild

but persistent bitter taste. Alcoholic solution of the substance did not give any coloration of precipitate with ferric chloride.

Further work in this direction is in progress.

My best thanks are due to Dr. S. Dutt for the kind interest he has taken in this work and to the 'Kanta Prasad Research Trust' of the Allahabad University for a scholarship which enabled me to take part in the investigation.

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ON TWO NEW SPECIES OF THE GENUS *CEPHALOGONIMUS*  
POIRIER FROM WATER-TORTOISES OF ALLAHABAD WITH  
REMARKS ON THE FAMILY *CEPHALOGONIMIDÆ* NICOLL.

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INTRODUCTION.

The genus *Cephalogonimus* was created by Poirier in 1886 for *Cephalogonimus lenoiri* parasitic in the intestine of an African turtle, *Tetrathya vallantii*. The most striking feature of this genus is the position of the genital pore at the extreme anterior end of the body on the dorsal surface in the region of the oral sucker. The genus comprises seven species, of which four are recorded from the reptilia and three from the amphibia. Looss recorded in 1899 the existence of the type species, *C. lenoiri* in *Trionyx nilotica* in Egypt. He also created in the same paper the sub-family *Cephalogoniminæ* to include *Cephalogonimus* and *Emoleptalea* which he defined. Stafford in 1902 described the species *C. americanus* from the intestine of *Rana virescens* and *R. clamata*, the common frogs of North America. Blazoit in 1910 added a third species, *C. europæus* which he obtained from the intestine of the European frog, *Rana esculenta*. Lühe in 1911 found a species in the intestine of the grass snake, *Tropidonotus natrix*, of which he did not give a description. Soon after in 1912 *C. vesicaudus* was found in the intestine of soft-shelled turtles (*Amyda* and *Aspidonetes*) and described by Nickerson. The fifth species, which was named *C. amphiumæ* by Chandler (1923), was obtained from the intestine of a male Urodele, *Amphiuma means* in the United States. Stunkard in 1924 described *C. compactus*, collected from the intestine of *Pseudemys floridana* in the United States. Moghe in 1930 recorded for the first time a species belonging to this genus from India, which he described as *C. emydalis* from the digestive tract of *Emyda granosa*, now called *Lissemys punctata*. The following four species, i.e., *C. ovatus* (Rudolph, 1803), *C. pellucidus* (V. Linstow, 1873), *C. trachysauri* (MacCallum, 1921) and *C. retusus* (Dujardin, 1845 and Odhner 1910), previously assigned to this genus have been removed from it. *C. ovatus* and *C. pellucidus* are now well known as belonging to the genus *Prosthogonimus*. Chandler (1923) excluded *C. trachysauri* from *Cephalogonimus* and also pointed out in the same paper that *C. retusus* and *C. europæus* were identical, a view which was later confirmed by Stunkard (1924).

As mentioned above the sub-family *Cephalogoniminæ* was created by Looss in 1899 for the genera *Cephalogonimus* and *Emoleptalea*. Nicoll in 1914 founded a new species of *Prothogonimus*, *P. vittellatus*, which he placed under the family *Cephalogonimidae*. This was the first time when the family name *Cephalogonimidae* appeared. It was therefore apparent that the sub-family *Cephalogoniminæ* Looss was raised to the rank of a family by Nicoll, who, however, did not give the family diagnosis. Later in 1924 he placed *Cephalogonimus* under the family *Prosthogonimidae*, which he founded to include the sub-family *Prosthogoniminæ* Lühe, but without diagnosis. Nicoll evidently considered the genus *Prosthogonimus* closely related to *Cephalogonimus* and hence included both these genera in the same family, first in his *Cephalogonimidae* (1914) and then *Prosthogonimidae* (1924). In a later paper (1926) he considered both these families as synonymous. Ward in 1917 placed the genus *Cephalogonimus* in the sub-family *Prosthogoniminæ*. Odhner (1911), after discussing the systematic position, came to the conclusion that the genus *Prosthogonimus* belonged to the family Lepodermatidae. Poche in 1925 followed Odhner in assigning the latter genus to the Lepodermatidae and accepted the family *Cephalogonimidae* Nicoll for *Cephalogonimus* and *Emoleptalea*, the genera originally included in the sub-family *Cephalogoniminæ* Looss.

The distomes described in this paper belong to new species of the genus *Cephalogonimus* and were obtained from the water-tortoises at Allahabad by Dr. H. R. Mehra, whom my best thanks are due for giving me these worms to study and describe. I am also much indebted to him for valuable help and guidance in this work, which was done under his close supervision.

As will be seen from the discussion given at the end of this paper, I am of opinion that the family *Cephalogonimidae* should be reduced to the rank of the previously known sub-family *Cephalogoniminæ* Looss within the family Lepodermatidae. In the general topography of organs the genus *Cephalogonimus* resembles closely the Lepodermatidae. The only important feature in which it differs is the position of the genital pore at the extreme anterior end of the body. But as will be seen from the discussion, the forward position of the genital pore can be explained to be due to a more forward shifting of the latter, and a greater elongation of the cirrus-sac than in some members of Lepodermatidae, as for instance, the Reniferinæ. In the genus *Emoleptalea* the genital pore lies a little behind anterior end to the right side of the oral sucker.

#### ***Cephalogonimus mehri*, n. sp.**

A large number, more than one hundred specimens of this species were obtained by Dr. H. R. Mehra from the small intestine of two specimens of soft-shelled tortoises *Lissemys punctata* in September 1930. These tortoises were also found infected with *Astiotrema gangeticus* Harshe. I was, however, unsuccessful in getting this species from the six specimens of *Lissemys punctata* dissected by me during the winter months of 1931.



The distomes are somewhat conical in shape with a broad nearly rounded anterior end and a bluntly pointed posterior end. They are small in size measuring 1.0–1.9 mm. in length and 0.42–0.57 mm. in greatest breadth, which lies in the region of the intestinal bifurcation.

The cuticle is studded, both on the dorsal and ventral surfaces of the body, with small spines, the finely pointed and hookshaped ends of which are directed backwards. On the dorsal surface the spines extend backwards up to the region of the anterior testis, but on the ventral surface they are present throughout the entire length, except a small posterior terminal part. Their absence in the posterior part of the body is probably due to a great proportional growth of the post-acetabular region just before sexual maturity. They are large in number, densely crowded in close set rows in front of the acetabulum especially around the oral sucker, where they are smaller in size and not sharply pointed.

The suckers are nearly spherical in outline. The oral sucker is a little larger than the ventral, measuring 0.13 to 0.16 mm in diameter. It lies subterminally with its opening directed towards the ventral surface. The ventral sucker, 0.1 to 0.15 mm. in diameter, is situated at 0.26 to 0.45 mm. distance, *i.e.*, one-fourth length of the body, behind the anterior end. The measurements of the body, given in the following table, will indicate its exact position.

TABLE I

| Specimen. | Length of body in front<br>of the ventral sucker<br>(in mm.). | Length of body behind the<br>ventral sucker<br>(in mm.). |
|-----------|---|--|
| 1         | 0.26  | 0.75   |
| 2         | 0.39  | 0.92   |
| 3         | 0.37  | 0.9  |
| 4         | 0.34  | 1.1  |
| 5         | 0.45  | 1.5  |

The mouth lies at the bottom of the oral sucker and opens into a small, thin-walled prepharynx. The muscular pharynx is oval in outline and is provided with four lobes around its anterior margin. It measures 0.06–0.08 mm. in size and divides immediately into the intestinal caeca, the oesophagus being entirely absent. The intestinal caeca lie laterally occupying a position nearer the body wall than the median line and terminate generally a little behind the middle of the body, extending 0.05–0.07 mm. distance behind the posterior testis. They are nearly of equal length; only rarely is the right intestinal caecum slightly longer than the left one.

The excretory pore is situated terminally at the posterior end, slightly towards the ventral surface. It opens into a small spherical caudal vesicle, which is interposed between it and the excretory bladder. The caudal vesicle is surrounded by

a group of large parenchymatous cells with prominent nuclei. Its wall is characteristically infolded—the infoldings dividing the cavity, which is continuous in front with that of the median stem of the bladder. The excretory bladder is Y-shaped with the long main stem situated more towards the dorsal side and bifurcating close behind the posterior testis into two small cornua, which extend forwards as far as the middle of the anterior testis. The main stem is wider anteriorly and posteriorly, and is provided with three small diverticula on each side. The cornua are of fairly large diameter and situated internal to the intestinal caeca in the region of the posterior testis, but dorsal to them in the region of the anterior testis.

The genital opening is situated at the anterior end of the body in the mid-dorsal line in front of the oral sucker.

The testes lie obliquely close behind each other, posterior to the ventral sucker, in the second quarter of the body. They are nearly spherical with entire margins; the posterior testis, which lies in the median plane in the middle of the body length, is usually slightly larger, measuring 0.14–0.21 mm. in diameter. The anterior testis is situated to the left side, *i.e.*, the side opposite to the ovary and measures 0.14–0.17 mm. in diameter. In a few specimens, however, the anterior testis was more broad than long. The vasa efferentia are long thin tubes which arise from the middle of the anterior margin of the testes. The cirrus-sac is large, fusiform and somewhat curved in an S-shaped manner, having thick muscular walls, composed mainly of longitudinal muscle fibres. Its basal end lies in front of the ovary to the right side of the acetabulum and is slightly curved around the latter; sometimes it extends further backwards behind the middle of the ovary, pushing the intestinal caecum of the right side laterally towards the body wall. The cirrus-sac consists of a large sac-like basal portion, which lies obliquely between the acetabulum and the pharynx, and extends forwards to cross ventrally the intestinal caecum of the left side, and a distal long narrow tubular portion, which runs ventrally to the left side of the pharynx and turns dorsally round the oral sucker to open into the genital atrium. The vesicula seminalis is large and filled with sperms. It is situated in the basal part of the cirrus sac and is deeply constricted so as to be divided into two parts—a saccular proximal part occupying the entire space within the basal end of the cirrus sac, and elongated narrower coiled distal part which passes by a narrow duct into the pars prostatica. The pars prostatica of relatively great length has greater breadth proximally, where it is connected with the vesicula seminalis. The deeply staining prostrate gland cells occupy the entire space between the pars prostatica, the convoluted part of the vesicula seminalis and the walls of the cirrus sac.

The ovary, almost spherical in shape, is situated close behind the ventral sucker to the right side. It is smaller than the testes, measuring 0.11–0.15 mm. in diameter. The shell gland complex lies to its left close behind the ventral sucker between it and the anterior testis. The oviduct arises from the inner face of the ovary at its anterior end, and runs medially and slightly posteriorly to enter the shell

gland complex, where it becomes dilated to form the ootype. The ootype is situated more towards the dorsal side and is joined separately by the common vitelline reservoir, the duct of the receptaculum seminis, and pearshaped vesicle of the Laurer's canal. The receptaculum seminis is pearshaped or ovoid situated obliquely to the right side. Its posterior part lies immediately behind the ovary between the latter and the posterior testis. Its narrow anterior part passes towards the shell gland mass to open into the right side of the ootype. The Laurer's canal is broader forming a vesicle at its internal end, where it opens into the ootype at the end opposite to that at which the oviduct joins it. The Laurer's canal takes a backward S-shaped convoluted course, and runs dorsal to the receptaculum seminis to open to the exterior in the mid-dorsal line, in the region of the anterior testis by a minute pore, which is lined by cuticle continuous with that of the body wall. The uterus arises ventrally from the left side of the ootype. It extends backwards to the right side of the anterior testis and ventrally to the receptaculum seminis to reach the hinder end, where it turns forwards as the ascending uterus situated to the left side. The convolutions of the descending and ascending parts are symmetrically arranged and set distinctly apart in a regular manner in the right and left parts of the body, on each side of the main stem of the excretory bladder and ventrally to its cornua. The ascending uterus passes forwards between the shell gland complex and the ventral sucker taking a course parallel and dorsal to the cirrus-sac on its way to the genital atrium. The metraterm is absent.

The vitellaria are laterally situated in the body close to the outer side of the intestinal caeca. They are of limited extent consisting of only a few follicles 10—15 in number and extend from the intestinal bifurcation to the hinder end of the ovary. They terminate much in front of the hind ends of the intestinal caeca. The transverse vitelline ducts arise close behind the acetabulum and unite together to form the prominent vitelline reservoir, which enters the anterolateral side of the ootype.

The ripe ova are oval in shape and slightly yellowish in colour, measuring 0.0315—0.04 mm. in length and 0.018—0.022 mm. in breadth.

*Cephalogonimus mehri* differs from all the other species of the genus, which have the testes obliquely arranged behind each other, in the form of the body which is conical with the greatest width in the region of the intestinal bifurcation, in the short length of its vitellaria which commence in front of the acetabulum from the intestinal bifurcation and terminate at the posterior end of the ovary much in front of the hinder ends of the intestinal caeca, in the dorsal position of the ootype, in the presence of a pearshaped vesicle at the origin of the Laurer's canal and the host.

TABLE II  
Showing the characteristics of the species of the genus *Cephalogonimus*,  
having testes obliquely arranged behind each other.

|                 | <i>C. americanus</i><br>Stafford, 1902.  | <i>C. europaeus</i><br>Blazoit, 1910.                                    | <i>C. vesicaudus</i><br>Nickerson, 1912.  | <i>C. compactus</i><br>Stunkard, 1924.  | <i>C. melchri</i><br>n. sp.                                       |
|-----------------|--|--|---|---|---|
| Host . .        | <i>Rana virescens</i><br>and <i>R. clamata</i> .   | <i>Rana esculenta</i> .  | <i>Aspidonectes</i><br>and <i>Amyda</i> .   | <i>Pseudemys</i><br><i>floridana</i> .  | <i>Issememys</i><br><i>punctata</i> .                             |
| Size of suckers | Oral sucker larger than ventral sucker; size 0.26 by 0.24, 0.21 by 0.23.   | Oral sucker larger than ventral sucker; diameter 0.30, 0.20.             | Oral sucker smaller than ventral sucker; 0.22, 0.27.  | Both suckers of the same size; 0.09.  | Oral sucker larger than ventral sucker; 0.126—0.158, 0.105—0.147. |
| Oesophagus      | Present.   | Present.   | Absent.   | Present.  | Absent.   |
| Testes          | Spherical. Anterior to the left and posterior median in position.  | Spherical. Anterior to the left and posterior median.                    | Elongated transversely. Anterior to the left and posterior median.                                | Spherical. Anterior slightly to the left and posterior slightly to the right. | Spherical. Anterior to the left and posterior median.             |
| Ovary           | Almost spherical to the right, close behind ventral sucker.  | Spherical to the right of the hinder margin of ventral sucker.           | Subspherical close behind the ventral sucker, to the right.                                       | Almost spherical close behind ventral sucker.                                 | Spherical to the right of the posterior margin of ventral sucker. |
| Vitellaria      | Extend from half way between the ventral sucker and intestinal bifurcation to near the ends of intestinal caeca. | From intestinal bifurcation to a little in front of blind ends of caeca. | From half way between oral sucker and ventral sucker to the posterior border of posterior testis. | From a little in front of ventral sucker to the ends of intestinal caeca.     | From near intestinal bifurcation to hinder margin of ovary.       |
| Eggs . .        | 52 $\mu$ by 16 $\mu$   | 39 $\mu$ by 22 $\mu$   | 38 to 49 $\mu$ by 17 to 21 $\mu$ .  | 30 to 34 $\mu$ by 20 to 23 $\mu$ .  | 31 to 40 $\mu$ by 18 to 22 $\mu$ .                                |

***Cephalogonimus gangeticus*, n. sp.**

Thirty-five specimens of this species were obtained from the small intestine of one out of fifty specimens of *Trionyx gangeticus* examined by Dr. H. R. Mehra in 1930.

The distomes are small, measuring 4–5.3 mm. in length and 1.1–1.4 mm. in maximum breadth, which lies behind the posterior testis in the region filled with uterine convolutions. The body is elongated and somewhat elliptical, with the posterior end large and broadly rounded and the anterior end somewhat narrower.

The body wall is covered with spines, which hardly project out of the thick cuticle. The spines are thickly set and pointed at their outer ends. They are larger on the ventral surface of the body than on the dorsal surface, where they disappear entirely behind the ventral sucker. On the ventral surface they extend much further behind, but they are altogether absent near the posterior extremity.

The oral sucker is globular and lies subterminally at the anterior end. It is larger than the ventral sucker, measuring 0.26–0.32 mm. in diameter. The ventral sucker measures 0.24–0.28 mm. in diameter and is situated at about one-third distance from the anterior end of the body, as will be seen from Table I.

The mouth faces towards the ventral surface and opens into a thin-walled oesopharynx. The latter leads into a muscular pharynx of oval outline and 0.08–0.11 mm. length and 0.12–0.14 mm. breadth. The pharynx appears to be produced into four lobes at its anterior margin. A short oesophagus of 0.05–0.11 mm. length is present. The intestinal bifurcation lies far in front of the ventral sucker. The intestinal caeca terminate in front of the posterior end of the body at about the middle of the distance between it and the posterior testis.

The excretory pore is subterminal and ventral. It opens into a spherical caudal vesicle which lies between it and the excretory bladder. The walls of the caudal vesicle are produced inwards into folds, which divide its cavity into a corresponding number of pockets. The main stem of the excretory bladder lies in the median plane, pressed closely to the dorsal body wall. It divides immediately behind the posterior testis into the right and left cornua, which give it a Y-shaped appearance. The main stem receives behind the posterior testis, three lateral branches on each side which are subdivided into a number of finer tubes near the lateral margins of the body. The cornua of the bladder extend forwards outside the testes and the intestinal caeca, terminating at the middle of the ovary, where each divides into two branches. The latter extend forwards as far as the middle of vesicle seminalis and are branched throughout their course. The excretory system differs from that of *Cephalogonimus lenoiri* Poirier only in the presence of the caudal vesicle.

The genital pore lies at the end of a papilla situated at the extreme anterior end on the dorsal side in front of the oral sucker. The testes are situated one behind the other in the median plane of the body and are transversely elongated with entire or irregular margins. The anterior testis lies 0.64–0.73 mm. distance behind the ventral sucker and measures 0.23–0.38 × 0.4–0.58 mm. in size. The

posterior testis is situated 0.16–0.42 mm. distance behind the anterior testis, measuring 0.16–0.34 × 0.32–0.74 mm. The vasa efferentia arise from the middle of the anterior face of the testes and run forwards independently as narrow tubes right up to the base of the cirrus sac, where they unite to form a small inconspicuous vas deferens. The cirrus sac is large and fusiform, lying obliquely between the intestinal caeca, with the posterior end terminating immediately in front of the ventral sucker or extending up to the centrum of the latter. It has highly muscular walls composed mainly of longitudinal muscle fibres. It is narrow and tubular in its terminal part, which lies ventral to the left intestinal caecum, before it opens into the genital atrium. The vesicula seminalis occupies basal part of the cirrus sac and consists of two parts; a broad proximal part, which is covered by a thin layer of longitudinal fibres and a strongly coiled distal part having thick muscular walls. The pars prostatica and ejaculatory duct are long. The pars prostatica is lined by an epithelium of columnar cells surrounded outside by a layer of circular muscle fibres. The prostate gland cells form a huge mass filling entirely the intervening space between the distal part of the vesicula seminalis, pars prostatica and the walls of the cirrus sac. The protusible cirrus is small and unarmed.

The ovary is subspherical, measuring 0.28–0.36 × 0.24–0.32 mm. It lies to the right side immediately behind the ventral sucker with the outer margin touching right intestinal caecum. From its inner side about the middle of its length arises the oviduct, which after running towards the median line turns backwards to dilate into the ootype. The ootype is surrounded by a prominent shell gland mass of a smaller size than the ovary, which is situated about half way between the anterior testis and the acetabulum, somewhat nearer the former than the latter. The receptaculum seminis, ovoid in shape, measures 0.32–0.37 × 0.18–0.22 mm. in size. It is obliquely situated to the right between the ovary and the anterior testis and opens dorsally by a short duct into the ootype. The Laurer's canal is long and convoluted, lying ventral to the receptaculum seminis. It opens to the exterior on the dorsal surface of the body by a minute pore close in front of the anterior testis. Internally it joins the ootype near the posterior margin. The common vitelline reservoir opens ventrally into the ootype. The first convolution of the uterus arises from the left side of the ootype and passes a little forwards before it turns backwards to form a loop, which winds to the left side as the descending uterus in numerous irregular and closely packed convolutions up to the hinder end of the body. The ascending uterus is also highly convoluted and situated to the right side of the body parallel to the descending uterine convolutions. Sometimes the arrangement of the descending and ascending parts of the uterus is reversed, *i.e.*, the descending part is situated to the right and ascending to the left. As the entire post-testicular region is filled with uterine coils and lateral branches of the excretory bladder, the parenchyma is scarcely seen in this region. In front of the shell gland complex the ascending uterus passes dorsal to the ventral sucker and

the cirrus sac, terminating in the metraterm. The metraterm is well developed in this species, extending between the hinder end of the pharynx and the anterior end of the oral sucker. It opens to the right side of the male pore in the small genital atrium situated at the end of the genital papilla.

The vitelline glands are strongly developed commencing near the posterior end of the ventral sucker, and terminating at the posterior end or a little behind the posterior testis. They lie laterally, mainly in the extracaecal zone, but they also overlap the intestinal caeca extending inwards towards the median line. The two vitelline ducts, one from each gland, pass transversely anterior to the cephalic testis, where they unite in the median line to form the common vitelline reservoir, which discharges into the ootype.

The ripe eggs are oval in shape and yellowish in colour, measuring 0.024–0.028 mm. in length and 0.015–0.019 mm. in breadth.

*O. gangeticus* resembles the type species, *O. lenori* Poirier, in the subterminal position of the oral sucker, excretory system, fusiform shape of the cirrus-sac, position of the ovary to the right side of the ventral sucker and the uterus having a characteristic loop at its commencement. But it differs in the larger size of its body, in having the oral sucker larger than the ventral sucker, presence of a caudal vesicle at the end of the excretory bladder, position of the ventral sucker at one-third distance from the anterior end, shape and size of the testes, larger size of the receptaculum seminis, absence of a pear-shaped vesicle at the origin of the Laurer's canal, asymmetrical arrangement of the uterine convolutions and greater length of the vitellaria.

*O. gangeticus* also resembles *O. amphiumae* Chandler, in having body of nearly same size and the maximum width in the post-testicular region, subterminal position of the oral sucker and its larger size than that of the ventral sucker, possessing a caudal reservoir at the end of the excretory bladder, asymmetrical arrangement of the uterine coils and great length of vitellaria. But it differs remarkably in the size of the suckers, ventral sucker being more posterior than in *O. amphiumae*, oesophagus intermediate in length between that of *O. amphiumae* and *O. lenoiri*, in the shape and position of the testes and the cirrus sac, size and shape of the receptaculum seminis, which opens into the ootype dorsally instead of ventrally as in *O. amphiumae* and the host.

The new species also resembles, in a few features, *O. emydales* Moghe, such as the presence of a caudal vesicle, oral sucker being larger than the ventral sucker, testes transversely elongated, the vitellaria extending from the level of the ventral sucker to a point behind the posterior testis. But the important points, in which *O. gangeticus* differs from *O. emydales*, are larger size of the body, subterminal position of the oral sucker, acetabulum situated more towards the posterior end, presence of an oesophagus, cirrus sac not coiled on itself near the intestinal bifurcation as in *O. emydales*, larger size of the testes and ovary, position of the ovary to the right side and not immediately behind the ventral sucker, larger size

and oval form of the receptaculum seminis, uterine coils passing ventrally and not laterally to the testes and the vitellaria overlapping the intestinal caeca instead of being restricted to the lateral fields of the body.

The above-mentioned differences are prominent enough to justify the creation of a new species, for which I give the following diagnosis:

Spines on the dorsal side restricted to the preacetabular region; oral sucker larger than the ventral sucker and situated at one-third distance from anterior end; short oesophagus present; caudal vesicle of the excretory bladder having infolded walls; testes transversely elongated and of large size situated in second-third of the body; cirrus sac fusiform, terminating near the centrum of the ventral sucker; ovary subspherical, situated to the right side of the ventral sucker; shell gland complex to the left side of the ovary; uterine convolutions passing ventral to the testes; metraterm present; genital pore at the end of a protrusible papilla on the dorsal side in front of the oral sucker; eggs oval and yellowish, measuring 0.024–0.028 mm. in length and 0.015–0.019 mm. in width. Host. *Trionyx gangeticus*. Locality Allahabad.

TABLE III

Dimensions in mm. of specimens of *C. gangeticus*, n. sp.

| Specimen. | Size of body.     | Length in front of the ventral sucker. | Length behind the ventral sucker. | Diameter of oral sucker. | Diameter of ventral sucker. | Size of pharynx.  | Size of anterior testis. | Size of posterior testis. | Size of ovary.    | Size of receptaculum seminis. |
|-----------|-------------------|--|-----------------------------------|--------------------------|-----------------------------|-------------------|--------------------------|---------------------------|-------------------|-------------------------------|
| 1         | 5.32<br>x<br>1.21 | 1.72                                   | 3.6                               | 0.3                      | 0.28                        | ...               | 0.38<br>x<br>0.51        | 0.32<br>x<br>0.74         | 0.36<br>x<br>0.32 | 0.37<br>x<br>0.19             |
| 2         | 5.08<br>x<br>1.11 | 1.71                                   | 3.37                              | 0.28                     | 0.26                        | 0.11<br>x<br>0.13 | 0.27<br>x<br>0.58        | 0.26<br>x<br>0.63         | 0.36<br>x<br>0.3  | 0.32<br>x<br>0.19             |
| 3         | 4.27<br>x<br>1.15 | 1.34                                   | 2.93                              | 0.26                     | 0.24                        | ...               | 0.3<br>x<br>0.4          | 0.34<br>x<br>0.58         | 0.28<br>x<br>0.24 | ...                           |
| 4         | 5.08<br>x<br>1.37 | 1.72                                   | 3.34                              | 0.32                     | 0.27                        | 0.11<br>x<br>0.14 | 0.37<br>x<br>0.37        | 0.32<br>x<br>0.32         | 0.36<br>x<br>0.31 | 0.32<br>x<br>0.22             |
| 5         | 4.85<br>x<br>1.15 | 1.61                                   | 3.24                              | 0.3                      | 0.27                        | 0.11<br>x<br>0.44 | 0.3<br>x<br>0.53         | 0.21<br>x<br>0.7          | ...               | 0.37<br>x<br>0.21             |
| 6         | 4.0<br>x<br>1.5   | 1.28                                   | 2.72                              | 0.26                     | 0.24                        | 0.08<br>x<br>0.12 | 0.23<br>x<br>0.51        | 0.16<br>x<br>0.69         | 0.28<br>x<br>0.32 | 0.33<br>x<br>0.18             |



TABLE IV  
Showing diagnostic characters of the species of the genus *Cephalogonimus* having testes in tandem.

|                 | <i>C. lenoiri</i><br>Poirier, 1886.   | <i>C. amphiumae</i><br>Chandler, 1923.  | <i>C. emydalis</i><br>Moghe, 1930.  | <i>C. gangeticus</i><br>n. sp.  |
|-----------------|---|---|---|---|
| Host            | <i>Tetrathra vallanti</i> .   | <i>Amphiuma means</i> .   | <i>Emyda granosa</i> .  | <i>Trionyx gangeticus</i> .   |
| Body length     | 3.0   | 4.4-5.3.  | 1.87-2.15.  | 4.0-5.32.   |
| Maximum width   | 1.0 at level of female genital organs.  | 1.22-1.30 in third-fifth of body behind posterior testis  | 0.6-0.73 at level of anterior testis.   | 1.11-1.37.  |
| Size of suckers | Oral sucker subterminal, smaller than ventral sucker, which is situated a little in front of middle of body; diameter 0.24; 0.29. | Oral sucker subterminal larger than ventral, which is placed at two-sevenths of body length from anterior end; diameter 0.42-0.43, 0.368-0.38.  | Oral sucker terminal, larger than ventral, which lies in anterior fourth of body; diameter, 0.168, 0.137.   | Oral sucker larger than ventral sucker, which lies at one-third body length from the anterior end; diameter 0.26-0.32; 0.24-0.28. |
| Pharynx         | Breadth 0.16, and length 0.11.  | Diameter 0.192.   | Diameter 0.092.   | Breadth 0.12-0.14 and length 0.08-0.11.   |
| Oesophagus      | Present, length 0.15.   | Barely distinct.  | Absent.   | Short, length 0.05-0.11   |
| Testes          | Ovoid and simple, in the first part of second-half body.  | Nearly rounded; in contact. Diameter of anterior 0.41-0.48 and posterior 0.30-0.47.   | Transversely elongated. Anterior measures 0.146-0.198 by 0.2-0.225, and posterior 0.123-0.156 by 0.19-0.23. | Transversely elongated. Anterior 0.23-0.38 by 0.4-0.58; posterior 0.16-0.34 by 0.32-0.74.   |
| Cirrus sac      | Fusiform, lying obliquely between intestinal caeca.   | Long and flask-shaped, lying obliquely between intestinal bifurcation and ventral sucker.   | Large, lying obliquely between intestinal caeca, coils once on itself near intestinal bifurcation.          | Fusiform, lying obliquely between intestinal caeca.   |
| Ovary           | Spherical, just behind ventral sucker, to its right, nearly in the middle of body.  | Spherical, immediately posterior to ventral sucker, slightly to its right with its centre about one-third of the body length from anterior end. | Nearly round, lies just behind ventral sucker and slightly anterior to middle of the body.                  | Subspherical, immediately posterior to ventral sucker, to its right.  |

TABLE IV — (contd.)

|                         | <i>C. lenoiri</i><br>Pointier, 1886. | <i>C. amphistomae</i><br>Chandler, 1923. | <i>C. emydalis</i><br>Moghe, 1930. | <i>C. gangeticus</i><br>n. sp. |
|-------------------------|--------------------------------------|--|------------------------------------|--------------------------------|
| Receptaculum<br>seminis | ...                                  | ...                                      | ...                                | ...                            |
| Uterus.                 | ...                                  | ...                                      | ...                                | ...                            |
| Vitellaria              | ...                                  | ...                                      | ...                                | ...                            |
| Eggs                    | ...                                  | ...                                      | ...                                | ...                            |

Receptaculum  
seminis

Uterus.

Vitellaria

Eggs

Flaskshaped.

With symmetrical coils.

Follicles in anterior half  
of body behind ventral  
sucker.35 by 17  $\mu$ .

Flaskshaped.

Irregularly coiled.

Extend from a level just be-  
hind anterior end of the  
ventral sucker to level of  
posterior testis and on the  
left side the follicles are  
more extensive.26 by 13  $\mu$ .

Round.

Convulsions symmetri-  
cally arranged.Follicles commence at  
the level of the ventral  
sucker extending to a  
point mid way between  
testes and ends of in-  
testinal caeca, extent  
on left slightly long.27 by 11  $\mu$ .

Ovoid.

Irregularly coiled.

Begin near the posterior  
end of ventral sucker  
and extend up to pos-  
terior end of caudal  
testis or little behind  
it.24—28  $\mu$  by 15—19  $\mu$ .

KEY TO THE SPECIES OF THE GENUS *CEPHALOGONIMUS* POIRIER

The genus is divided into two groups on the basis of the testes, whether they lie in tandem or obliquely behind each other.

## GROUP I.

Testes in tandem, one behind the other.

- A. Oral sucker smaller than the ventral sucker . . . . . *C. lenoiri* Poirier, 1886.
- Oral sucker larger than the ventral sucker . . . . . B.
- B. Oesophagus absent . . . *C. emydalis*, Moghe, 1930. Oesophagus present. C.
- C. Testes nearly rounded, *C. amphiumae*, Chandler, 1923
- Testes transversely elongated *C. Gangeticus*, n. sp.

## GROUP II.

Testes placed obliquely behind each other Genital opening, at some distance behind anterior end on the dorsal side of oral sucker-A

- A. Genital pore median ... *C. americanus* Stafford, 1902.
- Genital pore lateral to the right side. .... *C. europaeus*, Blazoi, 1910.
- Genital pore situated at the anterior tip of the body. .... B.
- B. Oral sucker smaller than ventral sucker. .... *C. vesticaudus* Nickerson, 1912.
- Both suckers of the same size. *C. compactus* Stunkard, 1924.
- Oral sucker larger than ventral sucker . . . *C. mehri*, n. sp.

**Discussion on the Systematic position of the family Cephalogonimidae.**

The family Cephalogonimidae resembles the family Lepodermatidae in the following characters:—

- (1) Cuticle spinose.
- (2) Prepharynx, pharynx and oesophagus present.
- (3) Excretory bladder typically Y-shaped, with long median stem and two short lateral diverticula.
- (4) Ovary in front of the testes, behind the acetabulum and usually to the right side.
- (5) Testes usually near middle of the body, obliquely or directly behind each other.
- (6) A muscular cirrus sac containing seminal vesicle, pars prostatica, prostate gland cells and a cirrus.
- (7) Uterus highly convoluted, filling the posterior half of the body, generally arranged as descending and ascending parts to the right and left sides.
- (8) Yolk glands of varying length restricted to the sides of the body.

The topography of organs in the genera *Cephalogonimus* and *Ethioleptalea* are so similar to that in the family Lepodermatidae that it is hardly possible to separate them from that family. The only characters, which appear to distinguish them from the Lepodermatidae are:—

- (1) Position of the genital pore at the extreme anterior end of the body.

- (2) Bifurcation of the main stem of the excretory bladder immediately behind the posterior testis and not in front of the testes as in the Lepodermatidae.
- (3) Branched condition of the main stem as well as the cornua of the excretory bladder.
- and (4) Uterine coils passing ventrally or laterally to the testes and not between them as in the latter family.

But these characters are not of such systematic importance as to justify the creation of the family Cephalogonimidae. On the other hand, it appears that all of them except the first one are also met with in certain genera of the Lepodermatidae.

In the genera *Renifer* Pratt, *Ochetosoma* Braun, *Lechriorchis* Stafford of the sub-family *Reniferinae* Pratt, the genital pore occupies an extreme lateral and forward position, i.e., near the pharynx and the cirrus sac is long extending to the centrum of the ventral sucker. In the genera *Mediorima*, *Dasymetra*, *Platymetra* and *Xenopharynx*, which Mehra includes in the *Reniferinae*, the genital pore is median close behind or on the intestinal bifurcation. Mehra considers these genera to be the primitive *Reniferinae* combining in themselves with the typical characters of the *Reniferinae*, certain primitive features which are met with in the genus *Styphlodora*. He takes a form like *Styphlodora* to represent the basis of evolution from which the *Reniferinae* have arisen through such intermediate forms as *Mediorima* and *Dasymetra*. Proceeding on the same evolutionary hypothesis, we can derive the terminal position of the genital pore of the Cephalogonimidae if we imagine that the genital pore of such forms as *Renifer* and *Ochetosoma* has become shifted further forwards so as to lie at the extreme anterior end and the cirrus sac has become much more elongated and narrowed in its terminal part than in the typical Lepodermatidae. It is well known that the position of the genital pore varies considerably in the family Lepodermatidae and it should not be surprising if in certain genera such as *Cephalogonimus* it has come to occupy an extremely anterior position, i.e., in front of the oral sucker. In the genus *Emoleptalea* the genital pore lies to the right side of the oral sucker. Even in the genus *Cephalogonimus* the position of the genital pore varies. In the two species, *C. americanus* and *C. retusus*, it lies either median or to the side, on the dorsal side of the oral sucker, a little distance behind the anterior end; whereas in all the other species of the genus it lies further forwards at the extreme anterior tip of the body. It is evident that former condition is primitive indicating a further forward shifting of the pore than in the typical *Reniferinae*.

It may be pointed out that in the genera *Prosthogonimus* and *Schistogonimus* the genital pore lies near the extreme anterior end to the left side of the oral sucker and the cirrus sac does not extend as far as the ventral sucker but it terminates a little behind the intestinal bifurcation. In *Prosthogonimus anatinus* the male genital duct opens on a papilla near the anterior end of the oral sucker. The condition in *Prosthogonimus* confirms the view that with the gradual shifting

forward of the genital pore the relation of the basal part of the cirrus sac with the acetabulum has become correspondingly changed.

The presence of lateral branches in the excretory bladder is a character not peculiar to Cephalogonimidae. We also find the main stem and the cornua provided with lateral branches in several genera of the family Lepodermatidae. It was this character which led Baer to divide the Lepodermatidae Odhner into two families, Lepodermatidae and Reniferidae. Subsequent workers, among whom Poche and Mehra may be mentioned, have criticised this classification. It is therefore obvious that this character is not of such importance as to force us to retain the family Cephalogonimidae.

The bifurcation of the main stem of the excretory bladder behind the posterior testis should not be considered as an important difference between the two families. The main stem of the excretory bladder is considerably longer than the cornua in all the species of the genus *Cephalogonimus* as is the case in the Lepodermatidae. The bifurcation of the main stem of the bladder behind the testes in *Cephalogonimus* can be easily explained to be due to the crowding together of the testes, the ovary and the receptaculum seminis in the median plane of the body so as to leave practically no space for the main stem of the excretory bladder to extend forwards in that region. Hence the bifurcation of the main stem into cornua has taken place behind the testes, there being ample space on the lateral sides in that region for the cornua to proceed forwards in their course.

As the testes have come to lie very close together in the median plane leaving no space between them for the uterine coils to pass through in *Cephalogonimus*, the arrangement of uterine convolutions has consequently taken a slightly different course than in many Lepodermatidae in that descending and ascending parts of the uterus do not pass between the testes but ventrally or laterally to them, to fill the post-testicular region of the body.

In view of what has been said above it appears beyond doubt that the family Cephalogonimidae is untenable. This family should be reduced to the rank of a sub-family within the family Lepodermatidae Odhner. The sub-family Cephalogoniminæ resembles the sub-family Reniferinæ in the presence of spines on the integument; termination of the intestinal caeca at some distance in front of the posterior end of the body; the excretory bladder provided with lateral branches; tendency of the genital pore to shift more forwards towards the anterior end; cirrus sac having in its basal part a coiled vesicula seminalis, followed by a long tubular pars prostatica; position of the ovary and testis behind the ventral sucker and the configuration of the uterus.

Diagnosis of the sub-family Cephalogoniminæ Looss, 1899 (Cephalogonimidae Nicoll, 1914.):—

Lepodermatidae; small size: beset with spines in a part of or entire length of the body; oesophagus short or absent; excretory vesicle Y-shaped consisting

of a long median stem and short cornua, and provided with lateral branches; genital pore situated at extreme anterior end on the dorsal side or a little behind it in the region of the oral sucker; testes in tandem or obliquely situated one behind the other; cirrus sac long having a curved shape, containing a coiled vesicula seminalis and a long pars prostatica; ovary, spherical or sub-spherical, pretesticular, situated to the right side of the posterior end of acetabulum; receptaculum seminis and Laurer's canal present; uterus much convoluted filling post-testicular region with convolutions in ascending and descending parts to the right and left sides and passing ventral or lateral to the testes.

Parasites of amphibia, reptilia and birds.

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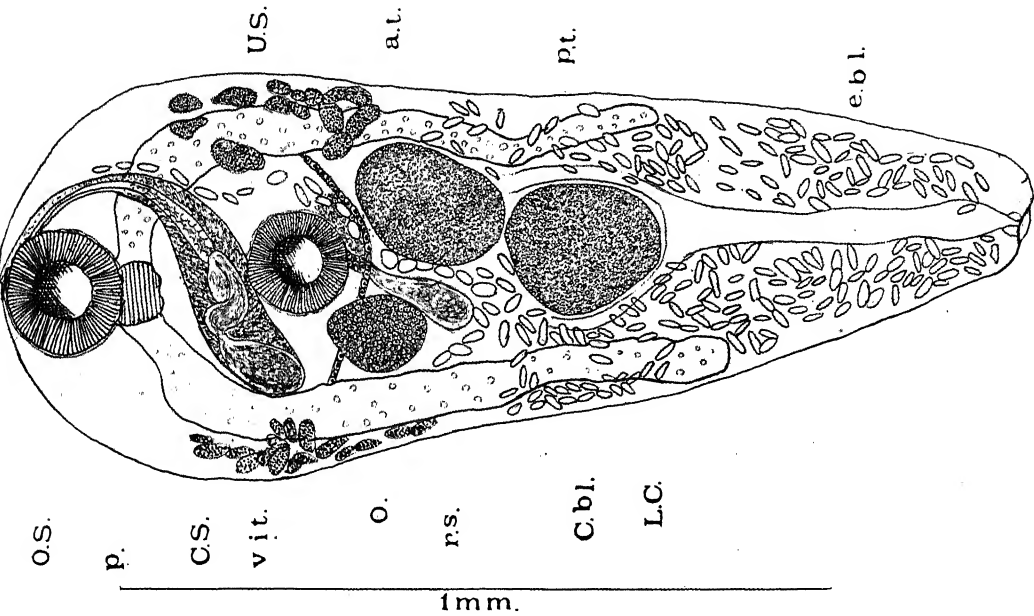


Fig. 1

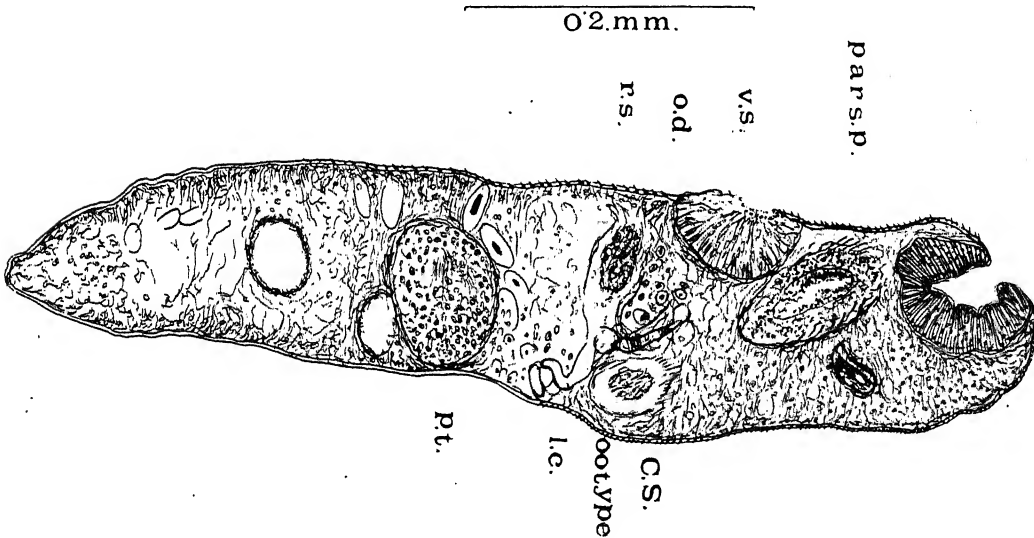


Fig. 2

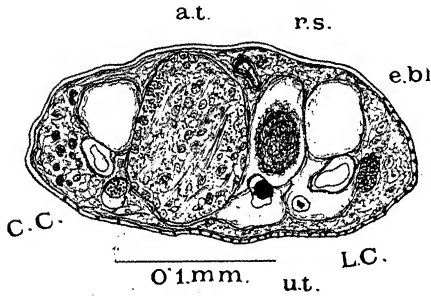


Fig. 3

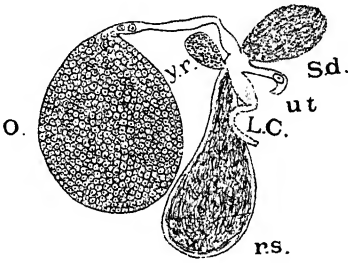


Fig. 4

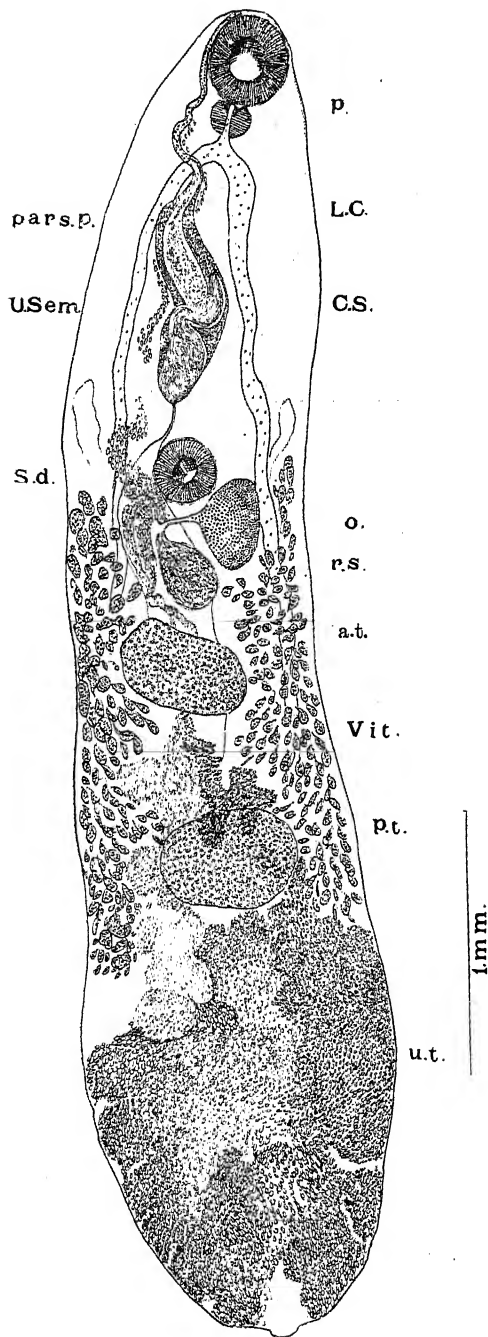


Fig. 5

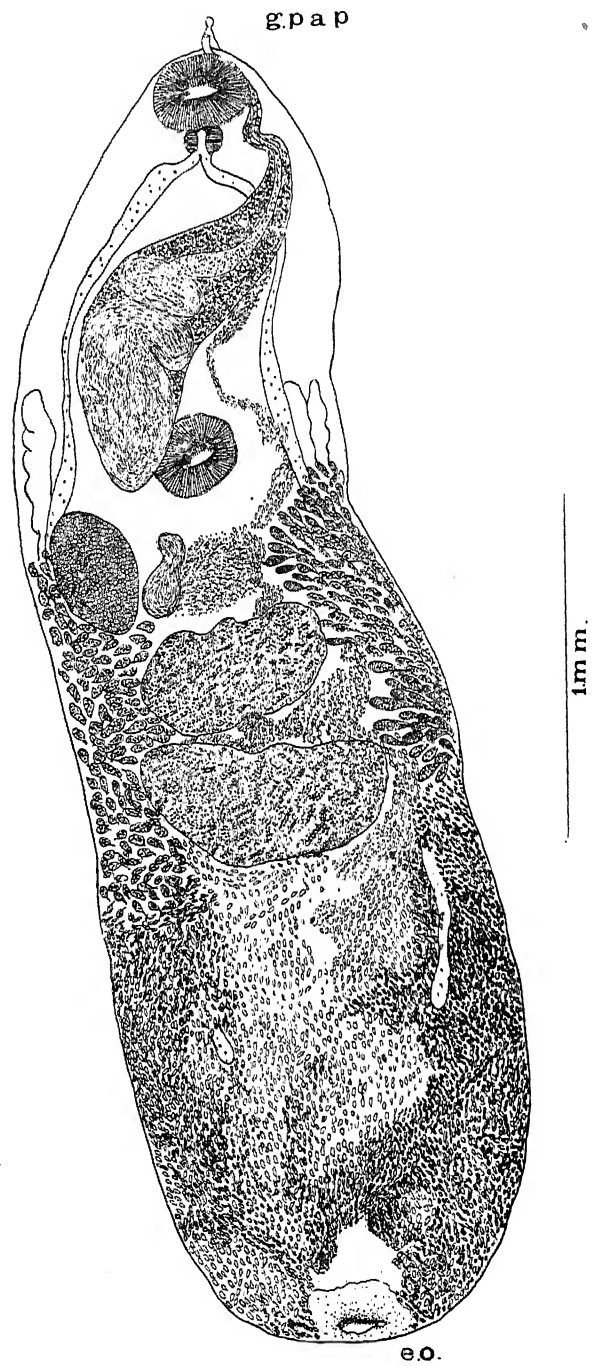


Fig. 6



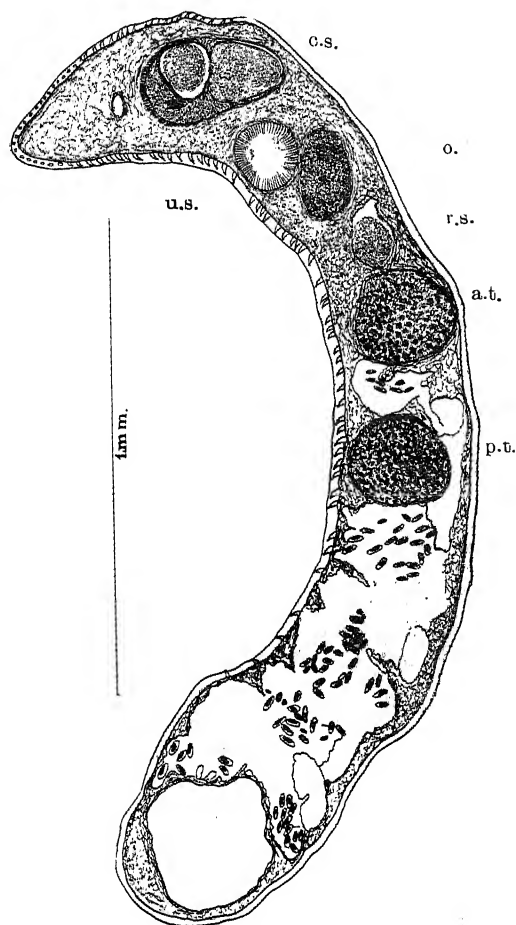


Fig. 7

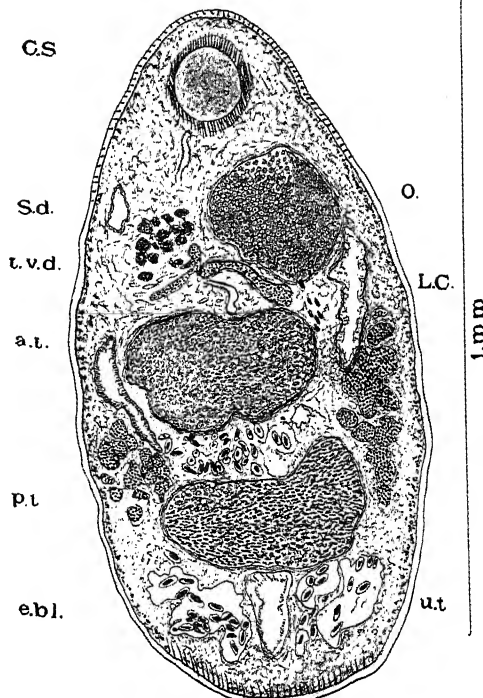


Fig. 8

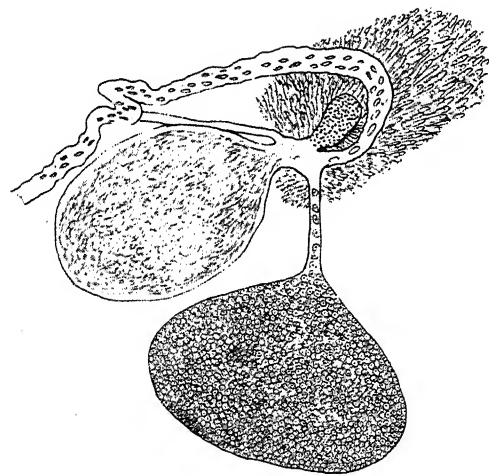


Fig. 9

EXPLANATION OF PLATES AND KEY TO LETTERING  
USED IN FIGURES

Figures 1—4. *Cephalogonimus mehri*.

1. Ventral view of a specimen.
2. Vertical-longitudinal section through posterior testis, Laurer's canal, receptaculum seminis and oviduct.
3. Transverse section through anterior testis, receptaculum seminis and Laurer's canal.
4. Diagrammatic view of female sexual organs constructed from a series of longitudinal sections.

Figures 5—9. *Cephalogonimus gangeticus*.

5. Dorsal view of a specimen.
6. Ventral view of a specimen.
7. Vertical-longitudinal section through testes, receptaculum seminis and ovary.
8. Horizontal-longitudinal section through testes, ovary, yolk reservoir and Laurer's canal.
9. Diagrammatic view of female sexual organs.

a. t., anterior testis; b. w., body wall; c. bl., cornua of bladder; c. s., cirrus sac; e. bl., excretory bladder; e. o., excretory opening; g. p., genital pore; g. pap., genital papilla; i. c., intestinal caecum; L. C., Laurer's canal; o., ovary; o. d., oviduct; oes, oesophagus; o. s., oral sucker; p., pharynx; p. p., prepharynx; pars. p., pars prostatica; pros., prostate gland; p. t., posterior testis; r. s., receptaculum seminis; s. g., shell gland; t. v. d., trans-vitelline duct; ut., uterus; v. e., vasa efferentia; v. s., ventral sucker; v. sem., vesicula seminalis; vit., vitellaria; y. r., yolk reservoir.

# SPECTRA OF TREBLY AND QUADRUPLY IONISED LEAD

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## SPECTRUM OF $Pb_{IV}$

The spectrum of trebly ionised lead was first investigated by Carroll,<sup>1</sup> but there were several points in his analysis which remained obscure. The recent accurate measurements of Arvidsson<sup>2</sup> for the spark spectra of lead in the Schumann region have been utilised in this paper to improve upon the existing analysis.

Carroll expressed doubt as to which of the two pairs

$$\lambda \ 1029, 1313$$

$$\text{and } \lambda \ 1049, 1313$$

may be identified as belonging to  $6s^2S-6p^2P$  transition. Arvidsson has shown that  $\lambda \ 1049$  belongs to  $Pb_{III}$  and this therefore establishes the identity of  $\lambda \ 1029, 1313$  as the fundamental pair, and is in conformity with the analysis of Rao and Narayan.<sup>3</sup>

Regarding the allocation of  $6p^2P-6p^2D$  lines, we have adopted the scheme of S. Smith,<sup>4</sup> as being most plausible, and this is also borne out by the experimental observations of Arvidsson. S. Smith has further identified the lines of higher transitions, viz. —

$$6d^2D-7p^2P$$

$$7s^2S-7p^2P$$

$$7p^2P-7d^2D$$

The first two multiplets are quite correct, but the identification of  $\lambda \ 2508.98, 3087.10$  and  $3145.60$  as  $7p^2P-7p^2D$  is not justified in the light of the data supplied by Arvidsson, and the lines  $2508.98$  and  $3145.60$  are here classified as belonging to  $7p^2P-8s^2S$  group. This is supported by the presence of the lines:

$$576.43 \ (2) \qquad 6p^2P_1-8s^2S$$

$$656.09 \ (2) \qquad 6p^2P_2-8s^2S$$

The lines  $\lambda \ 917.89$  and  $1137.86$  originate from  $6p^2P-7s^2S$  combination.

The revised list of  $Pb_{IV}$  lines so far classified is given in Table 1.

TABLE I

| $\lambda$ | I  | $\nu$   | Combinations          |
|-----------|----|---------|-----------------------|
| 1028.61   | 30 | 97218.6 | $6s\ ^2S_1-6p\ ^2P_2$ |
| 1313.06   | 40 | 76158.0 | $6s\ ^2S_1-6p\ ^2P_1$ |
| 917.89    | 7  | 10894.6 | $6p\ ^2P_1-7s\ ^2S_1$ |
| 1137.86   | 7  | 8788.4  | $6p\ ^2P_2-7s\ ^2S_1$ |
| 922.49    | 10 | 10840.2 | $6p\ ^2P_1-6d\ ^2D_2$ |
| 1116.08   | 7  | 8959.9  | $6p\ ^2P_2-6d\ ^2D_3$ |
| 1144.95   | 6  | 8734.0  | $6p\ ^2P_2-6d\ ^2D_2$ |
| 576.43    | 2  | 17348.2 | $6p\ ^2P_1-8s\ ^2S_1$ |
| 656.09    | 2  | 15241.8 | $6p\ ^2P_2-8s\ ^2S_1$ |
| 459.04    | 6  | 21784.6 | $6s\ ^2S_1-7p\ ^2P_2$ |
| 3002.78   | 2  | 33292.8 | $6d\ ^2D_2-7p\ ^2P_2$ |
| 3221.30   | 8  | 31034.4 | $6d\ ^2D_3-7p\ ^2P_2$ |
| 3962.45   | 6  | 25229.8 | $6d\ ^2D_2-7p\ ^2P_1$ |
| 4049.79   | 4  | 24685.7 | $7s\ ^2S_1-7p\ ^2P_1$ |
| 3052.66   | 7  | 32748.8 | $7s\ ^2S_1-7p\ ^2P_2$ |
| 2508.98   | 2  | 39844.8 | $7p\ ^2P_1-8s\ ^2S_1$ |
| 3145.60   | 2  | 31781.3 | $7p\ ^2P_2-8s\ ^2S_1$ |

Applying Hick's formula to the series  $6p^2P-n s^2S$  ( $n=6, 7, 8$ ) the value of the fundamental  $^2S$  comes out as 340186, giving an ionisation potential of 4.19 Volts. The terms of  $Pb_{IV}$  calculated on this basis are given in Table II.

TABLE II

|               | 6      | 7      | 8     |
|---------------|--------|--------|-------|
| $ns_1\ ^2S$   | 340186 | 155084 | 90544 |
| $np^2\ ^1F$   | 264028 | 130398 |       |
| $np^2\ ^3P_2$ | 242968 | 122335 |       |
| $nd^2\ ^3D_2$ | 155627 |        |       |
| $^2D_3$       | 153369 |        |       |

Arvidsson's list of  $\text{Pb}_{\text{III}}$  lines gives a number of strong lines between  $\lambda$  450 to  $\lambda$  600. These probably belong to the transition  $5d^{10} 6s^2 S - 5d^9 6s 6p^4$ ,  $^2(\text{FDP})$ . But the terms originating from the combination  $5d^9 6s 6p$  can be identified only by their combinations with the terms of the configurations  $5d^9 6s 6d$  or  $5d^9 6s^2 {}^2D$ . The data for the first transition is not available, and for the second, only partially. Attention, however, is directed to the presence of the following pairs with separation of about 21316.

|           |           |           |            |            |
|-----------|-----------|-----------|------------|------------|
| 92524 (3) | 95772 (3) | 98768 (3) | 112269 (8) | 118209 (3) |
| 71207 (1) | 74455 (4) | 77454 (2) | 90953 (1)  | 97893 (3)  |

It is possible that 21316 represents the  ${}^2D$ -separation of  $5d^9 6s^2$  combination, for it agrees well with the corresponding separations in  $\text{Au}_{\text{I}}$  (12274),  $\text{Hg}_{\text{II}}$  (15040) and  $\text{Tl}_{\text{III}}$  (18616).

SPECTRUM OF  $\text{Pb}_{\text{V}}$ 

Mack<sup>5</sup> has analysed about a dozen lines of  $\text{Pb}_{\text{V}}$ . He has obtained  ${}^3D_{3,2}$  and  ${}^1D_2$  terms of  $5d^9 6s$ , and  ${}^3P_2$ ,  ${}^1P_1$ ,  ${}^3F_{4,3,2}$  and  ${}^3D_3$  of  $5d^9 6p$  combination. With the help of Arvidsson's data it has been possible to extend the analysis and obtain many more terms. The separation  ${}^3D_3 - {}^3D_1$ , of  $5d^9 6s$  should be a little less than 22000 as derived from the sequence given in the following table:—

| <i>Element.</i>          | ${}^3D_3 - {}^3D_1$ |
|--------------------------|---------------------|
| $\text{Pt}_{\text{I}}$   | 10132               |
| $\text{Au}_{\text{II}}$  | 12728               |
| $\text{Hg}_{\text{III}}$ | 15556               |
| $\text{Tl}_{\text{IV}}$  | 18613               |

Since the separation of  ${}^3D_3 - {}^3D_2$  in  $\text{Pb}_{\text{V}}$  is 3936,  ${}^3D_2 - {}^3D_1$ , should be a little less than 18050. Several pairs with frequency interval 18007 have been obtained which fit in with the lines already analysed by Mack. The multiplets obtained are given in the table below.

TABLE III

| $5d^9 6s$<br>$5d^9 6p$ | $^3D_3$<br>3940           | $^3D_2$<br>18007         | $^3D_1$<br>3286                                 | $^1D_2$                  |
|------------------------|---------------------------|--------------------------|---|--------------------------|
| $^3P_2$<br>24687       | 84036·6<br>M* 1189·93 (9) | 80098·0<br>M 1248·47 (6) |   |                          |
| $^3P_1$<br>19930       |                           | 104785·<br>954·34 (7)    | 86775·0<br>1152·40 (1)<br>106705·<br>937·16 (3) | 83492·7<br>1197·71 (6)   |
| $^3P_0$                |                           |                          |   |                          |
| $^1P_1$                |                           | 113130·<br>M 883·94 (7)  | 95123·9<br>1051·26 (2)                          | 91838·3<br>M 1088·87 (5) |
| $^3D_3$<br>—9440       | 115742·<br>M 863·99 (15)  | 111807·<br>M 894·40 (8)  |   | 90514·1<br>M 1104·81 (3) |
| $^3D_2$<br>30524       | 106302·<br>940·72 (1)     | 102362·<br>976·93 (5)    | 84357·<br>1185·43 (8)                           | 81070·8<br>1233·48 (10)  |
| $^3D_1$                |                           | 132899·<br>752·51 (1)    | 114882·<br>870·45 (7)                           | 111598·<br>896·07 (7)    |
| $^1D_2$                |                           | 129955·<br>769·50 (5)    |   | 108664·<br>920·27 (7)    |
| $^3F_4$<br>—7839       | 110301·<br>M 906·61 (10)  |                          |   |                          |
| $^3F_3$<br>10779       | 102362·<br>976·93 (5)     | 98428·<br>1015·97 (1)    |   | 77134·<br>1296·43 (3)    |
| $^3F_2$                | 113141·<br>M 883·85 (7)   | 109204·<br>M 915·72 (9)  | 91197·<br>1096·52 (4)                           | M 87911·3<br>1137·51 (5) |

\* Lines followed by M are originally classified by Mack.<sup>5</sup>

The separations and the relative positions of the terms of the above combinations are as expected from the corresponding terms of the preceding elements.

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# A GENERALIZATION OF A WELL-KNOWN THEOREM

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The theorem known as Vivanti-Borel-Dienes-Theorem<sup>1</sup> asserts that if  $\sum C_n z^n$  has unit radius of convergence, and the  $O$ 's belong to a *Winkelraum* whose angle is less than  $\pi$  then  $z=1$  is a singular point of  $f(z)$  where  $f(z) = \sum C_n z^n$ . It may perhaps be a little interesting to know whether the *Winkelraum* referred to above can be replaced by a more general domain  $D$ . In the following theorem such a domain  $D$  is indicated; indeed, in a sense, it is a "best possible"  $D$ .

THEOREM.—Suppose that  $z=x+iy$ ,  $\delta$  and  $\Delta$  are any two positive numbers, and  $\theta$  is any angle; let  $D_1=D_1(\delta, \Delta)$  denote the domain which consists of the half plane,  $x \geq \delta$ , together with the region  $|y| \Delta \leq x$  for  $0 \leq x \leq \delta$ . Let  $D=D(\delta, \Delta, \theta)$  be the domain that  $D_1$  occupies when it has been rotated about the origin through an angle  $\theta$ . If now  $f(z) = \sum C_n z^n$  and the  $O$ 's are such that they belong to a  $D$ , and the Radius of Convergence of the power series is unity, then  $z=1$  is a singular point of  $f(z)$ .

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ON SOME EXPERIMENTS WITH IODINE VAPOUR

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The experiments described below were undertaken with the specific purpose of affording direct experimental verification of Franck's theory<sup>1</sup> of photo-dissociation of halogen molecules; though the experiments have not been successful, some results of very perplexing nature have been obtained, which may lead to some unexpected discovery.

It has been known from a long time that  $I_2$ -vapour at ordinary temperatures shows a band absorption beginning from  $\lambda 4995$  A. U. extending up to  $\lambda 3400$  A. U. The width of continuous absorption on both sides of  $\lambda 4995$  A. U. depends upon the total vapour content. Similar band and continuous absorption is also shown by the other halogens. The continuous absorptions have been explained by Franck in the following way:—

Iodine molecule in its normal state is supposed to consist of two iodine atoms in the lowest energy state, *i.e.*,  $5p^5 \cdot {}^2P_{3/2}$ . The next higher metastable state is  $5p^5 \cdot {}^2P_{1/2}$ . When light falls on a normal molecule, they act only on one of the electrons of the molecule so that  ${}^2P_{3/2}$ -state is excited to the next higher state, *viz.*, the  ${}^2P_{1/2}$  state. The excited molecule is now composed of two atoms of which one is



in the  ${}^3P_{\frac{3}{2}}$  and the other in the  ${}^2P_{\frac{1}{2}}$ -state. Franck postulates that we get the bands when the excited light is just sufficient to excite the atom from  ${}^3P_{\frac{3}{2}}$  to  ${}^2P_{\frac{1}{2}}$ -state, and thereby possesses sufficient energy to dissociate it. The situation is clearly explained by the Franck-Condon diagram showing the variation of potential energy with the distance between the component atoms in the normal and the excited states as explained in Fig. 1.

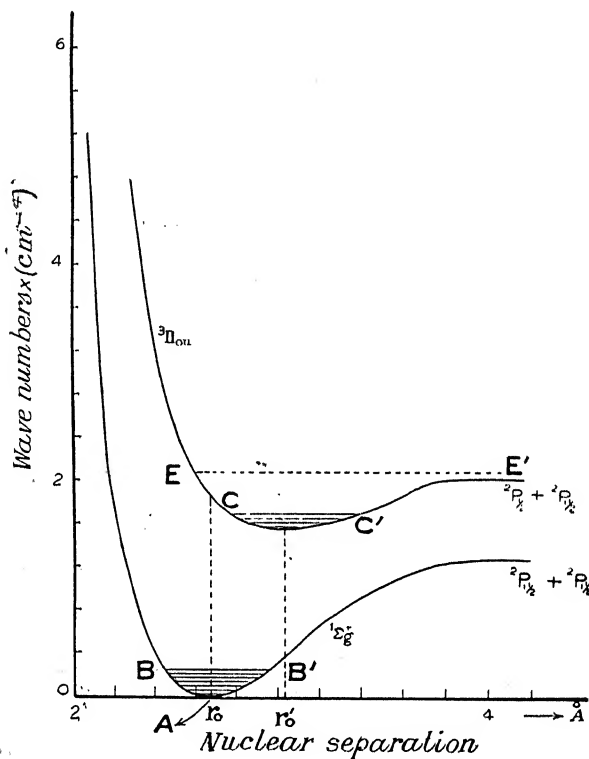


Fig. 1.—Franck-Condon diagram for energy states of the  $I_2$ -molecule.

The abscissæ represents distance  $r$  and the ordinates the potential energy  $U(r)$ . The minimum value of  $U(r)$  is taken as zero. The curve (1) shows the value of  $U(r)$  when the component atoms are in the  ${}^3P_{\frac{3}{2}}$ -state. In this case  $r_0 = 2.66 \times 10^{-8}$  cms. and  $\omega'' = 214.6 \text{ cm}^{-1}$

The lowest point A in curve (1) corresponds to the lowest vibration state  $n''=0$ . The upper points B B' corresponds to the excited vibrational states in which  $n'' > 1$

Curve (2) represents  $U(r)$  when the component atoms are in the  $^2P_{3/2}$  and  $^2P_{1/2}$ -states. In this case

$$r_0 = 3.08 \times 10^{-8} \text{ cm. and } \omega' = 127.5.$$

Here also the lowest point corresponds to the lowest vibration state of the excited  $n'=0$ . The higher points  $CC'$  correspond to higher vibration states in which  $n' > 1$ .

When light falls on the atom, the representative point may change from A to any point in curve (2). The most probable point of shift will be C, where C has the same nuclear distance  $r$  as A. But the molecule may change to any point lying on the curve (2). If such a point C lies above the line  $EE'$  which form the asymptote to the curve (2), iodine gets dissociated and the absorption now becomes continuous. If C be below  $EE'$  we get band absorption.

According to this theory the beginning of absorption indicates the photodissociation of the molecule of iodine into  $^2P_{3/2}$  and  $^2P_{1/2}$ -states. The truth of this theory is proved by the correctness of the mathematical relation

$$h\nu = D_{I_2} + ^2P_{3/2} - ^2P_{1/2}$$

We know from the spectroscopic data that

$$h\nu = 56.95 \text{ k cal. and } ^2P_{3/2} - ^2P_{1/2} = 21.6 \text{ k cal.}$$

Thus  $D_{I_2}$  comes out to be 35.35 k. calories.

This value is in agreement with Bodenstein and Starck's<sup>3</sup> value, which they obtained by direct experimental study of the degree of dissociation of  $I_2$  at different temperatures by the application of the law of mass action. If Franck's theory be correct, then as a result the illumination of  $I_2$  by light of wavelength less than  $\lambda$  4990, a good fraction of molecules should be expected to split up into atoms in  $^2P_{3/2}$  and  $^2P_{1/2}$ -states, and the number in the  $^2P_{1/2}$ -state should be equal to the number in the  $^2P_{3/2}$ -state.

The simplest way of experimentally demonstrating this is by studying the absorption spectrum of  $I_2$  vapour irradiated by light of wavelength less than  $\lambda$  4990. Irradiated iodine gas should show absorption of lines arising from  $^2P_{3/2}$  and  $^2P_{1/2}$ -states.

According to the classification of  $I_2$  arc lines by Turner,<sup>4</sup> Evans<sup>5</sup> and Deb,<sup>6</sup> the fundamental lines have been arranged as follows (Table 1):

According to Table 1 given below, irradiated  $I_2$  vapour is expected to show absorption of  $\lambda$  1830 and  $\lambda$  2062 lines respectively in the quartz region. Of this

$\lambda 1830$  indicates the presence of Iodine in  $^2P_{3/2}$ -state, and  $\lambda 2062$  indicates the presence of iodine in the  $^2P_{1/2}$ -state. In the existing literature several such experiments

Table 1

| $5p^5 \backslash 5p^4 6s$ | $^2P_{3/2}$               | $^2P_{1/2}$               |
|---------------------------|---------------------------|---------------------------|
| $^4P_{5/2}$               | 54632<br>$\lambda 1830.4$ |                           |
| $^2P_{3/2}$               | 56089<br>$\lambda 1782.9$ | 48494<br>$\lambda 2062.1$ |
| $^4P_{3/2}$               | 60885<br>$\lambda 1642.5$ | 53293<br>$\lambda 1876.4$ |
| $^2P_{1/2}$               | 61809<br>$\lambda 1617.9$ | 54216<br>$\lambda 1844.5$ |
| $^4P_{1/2}$               | 66342<br>$\lambda 1507.3$ | 58744<br>$\lambda 1702.3$ |

are reported. Turner and Samson<sup>6</sup> report that they were able to get the absorption of  $\lambda 1830$  and other lines corresponding to the  $^2P_{3/2}$ -state at a temperature of  $20^\circ\text{C}$ . When the same light was passed through  $\text{I}_2$  vapour at  $20^\circ\text{C}$  the absorption was found to be intensified when  $\text{I}_2$  vapour was irradiated with light from the carbon arc. But their experiments are rather indirect and indecisive, for it is difficult to see how vapour at  $20^\circ\text{C}$  in the absence of irradiation can be sufficiently dissociated to give absorption of the atomic line  $\lambda 1830$ . To show this, we calculate the degree of dissociation of vapour at  $20^\circ\text{C}$  from Gibson and Heitler's<sup>7</sup> formula; we find that

$$K_p = \frac{4x^2}{1-x^2} p = 1.23 \times 10^{-17}$$

and since the dissociation is extremely slight, we put  $1-x^2=1$ , and obtain

$$4x^2 n k T = 1.23 \times 10^{-17}.$$

$$\therefore x = 1 \times 10^{-10}$$

$$\left[ \text{since } n = \frac{p}{kT} = \frac{2.5 \times 10^{-1} \times 1330}{1.36 \times 10^{-16} \times 293} = 8 \times 10^{15} \right]$$

$\alpha$  represents the degree of dissociation at 20°C due to heat alone. But the pressure of Iodine at 20°C is about 0.25 mm. of mercury whence the number of iodine molecules per c.c. is  $8 \times 10^{15}$  as calculated above. Thus the number of free atoms per c.c. is

$$n\alpha = 8 \times 10^{15} \times 10^{-10} = 8 \times 10^5.$$

This number is quite insufficient to show any absorption  $I_2$  vapour.

Let us therefore carefully consider the experiments reported by Turner and Samson.<sup>8</sup> Discharge was passed through a tube containing iodine, which emitted the arc lines of iodine including  $\lambda 1830$ , and  $\lambda 2062$ . This light was passed through a second vessel containing iodine at 0.3 mm. pressure.

They found that on passing through the absorption chamber,  $\lambda 1830$  was absorbed feebly, but  $\lambda 2062$  was not absorbed at all. But when the latter was illuminated by light from a carbon arc  $\lambda 1830$  was still more strongly absorbed, while even in this case there was no trace of absorption of  $\lambda 2062$ . From this, they concluded that the increased absorption of  $\lambda 1830$  was due to photo-dissociation of  $I_2$  vapour, a conclusion with which it is difficult to agree, since no absorption of  $\lambda 2062$  was observed.

The experimental results are difficult to understand. According to the calculation given above,  $I_2$  at 20°C has only  $8 \times 10^5$  free atoms per c.c. and hence it cannot show any absorption of  $\lambda 1830$ . The absorption observed by Turner must have been due to some other cause. It may have arisen from the fact that, even in the first experiment, as  $I_2$  in the absorption chamber is subjected to continuous light from A, including emission lines between  $\lambda 4900$  and  $\lambda 4000$ , photodissociation of  $I_2$  is produced. The absorption of  $\lambda 1830$  must be due to iodine atoms produced in this way and when in the second experiment, the absorption chamber was subjected to light from carbon arc, photodissociation was still more intensified, hence  $\lambda 1830$  was still more strongly absorbed.

But this does not explain why  $\lambda 2062$  is not at all absorbed in any of the experiments. If the production of atoms was due to photodissociation,  $^2P_{1/2}$  atoms which are responsible for the absorption of  $\lambda 2062$  must have been produced in equal numbers with  $^2P_{3/2}$  atom which is responsible for the absorption of  $\lambda 1830$ , hence it is difficult to understand why  $\lambda 2062$  will not be absorbed in either case.

The difficulty may be explained by the assumption that  $^2P_{1/2}$  atoms after being produced are almost immediately reduced to the  $^2P_{3/2}$  state by collisions of the second type with the gas molecules present. Anyhow Turner and Samson have not been able to demonstrate the truth of Franck's theory. The same experiment was performed by Sponer and Watson<sup>9</sup> and they too report a negative result. The experiment was undertaken by me with a view to attack the problem directly and as the experimental procedure is somewhat different, it is described in detail below. I should mention here that when my experiments were started I was ignorant of the existence of these experiments.

### Experiment

The apparatus used in carrying out the present experiments was very simple. Continuous light from a hydrogen discharge tube was passed through a pyrex glass tube about 12 cm. long which was filled with iodine vapour coming from a bulb attached to it. The absorption tube was illuminated by means of carbon arc fed with metallic zinc. Zinc was used as it emits a strong triplet  $\lambda$ .

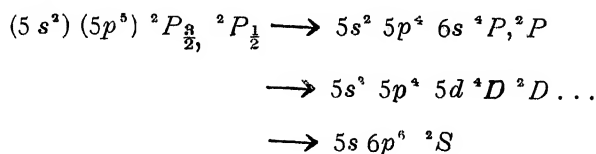
Both Schumann plates and ordinary plates sensitised by means of 0.5% solution of yellow vaseline in petroleum ether were used for photographing the absorption spectra. It was found that no trace of absorption of  $\lambda 2062$  could be seen in any case, but two new absorption lines were detected, the wavelengths of which were found to be  $\lambda 2012 \pm 1 \text{ \AA}$  and  $\lambda 1969 \pm 1 \text{ \AA}$ , respectively. These two lines appeared persistently in all plates whether the absorption chamber was irradiated by carbon arc or not.  $\lambda 1969$  was much fainter than  $\lambda 2012$ . In order to see whether these lines belonged to iodine present in the tube, another experiment was performed in which a mild discharge was passed through iodine contained in the absorption tube, which was provided with nickel electrodes. It was found that both these lines could also be obtained in the emission spectrum. On consulting the literature, it was found that FÜCHTBauer, Weibel and Holm<sup>10</sup> obtained two lines, whose wavelengths he gave as 2016 and 1972.3 Å.U. in a weak condensed discharge through iodine vapour. In addition to these he got various other lines between  $\lambda 2062$  and  $\lambda 1972$ . The two lines obtained by me seem to be identical with FÜCHTBauer's  $\lambda 2016$  and  $\lambda 1972$ , but the large discrepancy in wavelengths is inexplicable unless one of us has committed a grave error in measuring the lines.

Now these lines neither belong to silver, nickel or chlorine nor are air lines or principal lines of any element. The only alternative seems to be that they are due to the iodine-atom or iodine molecule or to some impurity present in the sample of iodine.

That these lines cannot be due to  $I_2$  molecule can be judged from the following reasons. The wavelength does not correspond to any of the band lines registered by Oldenberg<sup>11</sup> in this region. It may also be mentioned here that no band absorption was obtained in this region as reported by Kimura and others,<sup>12</sup> which may be due to the fact that the amount of iodine vapour present in the tube was very small as the temperature of the side bulb was maintained at  $0^\circ\text{C}$ .

Oldenberg bands correspond to the transition form  $5p^5 \text{ } ^2P_{3/2}$  to  $5p^5 6s^4 \text{ } ^1P_{1/2}$  states of one of the component atoms. The bands which are obtained in the  $\lambda 2000$  region are due to the fact that by heat the  $I_2$ -molecule in the fundamental state is raised to higher vibrational states, so that the bands shift towards the longer wavelength. The lines observed cannot possibly be identical with a narrow band absorption. This is further disproved by the fact that difference between the two lines observed on my plate is about  $\Delta\nu = 1086$  and has no relation to the fundamental difference  $\Delta\nu = 2136$  of the iodine molecule.

The next possibility is whether they can be due to any possible mode of transition of iodine atom. The fundamental state can pass by absorption to the states as mentioned below :



As regards the value of the  $5d$ -terms a comparison with the values of the corresponding terms in the neighbouring atoms from indium to caesium shows that their value cannot exceed 17000 (The value of  $cs\ 5d \ ^2D_{\frac{3}{2}}, \ ^2D_{\frac{1}{2}}$  are equal to 16807 and 16905 respectively). Hence lines due to the transition  $5p^5 \leftarrow 5p^4 5d$  will lie in the neighbourhood of  $\lambda\ 1500$ , for the value of  $5p^5 \ ^2P_{\frac{3}{2}} = 8500$  and  $5p^5 \ ^2P_{\frac{1}{2}} = 77000$ . Similarly the inner transition lines are also excluded because the value of  $^2S_{\frac{1}{2}}$  in such cases will be very small.

The only suggestion which can be made at this stage, but which is rather difficult to establish, is that they are due to element No. 85, which belongs to the halogen group. A number of investigators report the discovery of this element, but nothing seems to be certain. It is quite possible that in the sample of  $I_2$  this element is present in small proportion, and has not been separated by chemical methods used in the preparation of iodine. Three other samples of iodine were found to give  $\lambda\ 1212$ . In this connection, the case of discovery of Hafnium may be cited. Hafnium (72) is always associated with its analogue Zirconium (40), and lines of Hf were always found in the Zr-spectrum, but were disregarded as being merely due to impurities. It was only after Bohr indicated that Hf would have properties similar to Zr (40) and Hevesy and Coster established its existence by X-ray methods in Zirconia minerals, that the impurity lines in Zr-spectrum were traced to Hf (72). The spectrum of this element (85) will be quite similar to iodine and these two lines obtained by me may form the fundamental lines of the new element corresponding to the following transition.

Table 2

| $7p^5$              | $^2P_{\frac{3}{2}}$ | $^2P_{\frac{1}{2}}$ |
|---------------------|---------------------|---------------------|
| $7p^4 8s$           |                     |                     |
| $^4P_{\frac{5}{2}}$ | 2016                |                     |
| $^4P_{\frac{3}{2}}$ | 1970                |                     |

The facts of the experiments are not at least against such a hypothesis.

My thanks are due to Prof M. N. Saha, for his kind interest throughout the work.

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# ON THE ABSORPTION SPECTRA OF ALKYL HALIDES

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The explanation of the absorption spectra of the Alkyl Halides has received considerable attention from various authors, *e.g.* Herzberg and Scheibe<sup>1</sup>, Iredale and Wallace<sup>2</sup>, and Iredale and Mills<sup>3</sup> in recent years. In the region of quartz they have been found to possess no band absorption but there is a continuous absorption beginning from a long wave limit. It is well known that by an extension of Kratzer's theory of diatomic molecule, when about to dissociate, Born and Franck have shown in the case of ionic compounds like the halides of the alkalis, that the passage of continuous light through the vapours of these molecules results in photochemical dissociation into alkali and halogen, giving a continuous absorption



It is supposed as already mentioned that normally NaCl exists as  $\text{Na}^+$  and  $\text{Cl}^-$  and the primary act of light is to transfer one electron from Cl to Na, resulting in photochemical dissociation of the compound into two neutral atoms. Here  $h\nu$  can be obtained with the aid of a Born cycle as

$$h\nu = Q + \frac{1}{2}D_{\text{Cl}_2} + L_{\text{Na}} - L_{\text{NaCl}}$$

Where

$Q$  = Heat of formation of NaCl

$D_{\text{Cl}_2}$  = Heat of dissociation of Cl

$L_{\text{Na}}$  = Heat of sublimation of Na

$L_{\text{NaCl}}$  = Heat of sublimation of NaCl.

In the following table is reproduced the values obtained by Herzberg and Scheibe<sup>1</sup> for certain of the Methyl Halides.

Table 1

| Molecule               | Calculated limited<br>(k cal.) | Observed beginning and complete<br>extinction (k cal.) | Surplus energy after<br>accounting for the<br>excitation of<br>Halogen. |
|------------------------|--------------------------------|--|---|
| $\text{CH}_3\text{I}$  | 44                             | 102 (112)  | 37 (46)   |
| $\text{CH}_3\text{Br}$ | 59                             | 123 (143)  | 54 (76)   |
| $\text{CH}_3\text{Cl}$ | 73                             | 151 (164)  | 76 (89)   |



The second column gives the calculated energies of C-Cl bond. These values are given by Eucken (Lehrbuch der Chemische Physik) and have been calculated in the following way:—

Heat of formation of  $\text{CH}_4 = 368 \text{ k cal}$ ,

Heat of formation of  $\text{C}_2\text{H}_6 = 623 \text{ „}$

These give us four C-H bonds in  $\text{CH}_4$ , i.e.,  $4x = 368 \text{ k cal}^{\circ}$

so that  $x = 92 \text{ k cal}$

that is, energy of C-H bond  $= 623 \text{ „}$

In the case of  $\text{C}_2\text{H}_6$  we have six C-H bonds + one C-C bond  $= 623 \text{ k cal}$ .

value of C-C bond  $= 71 \text{ k cal}$ .

For  $\text{CH}_3\text{Cl}$  the heat of formation is  $349 \text{ k cal}$ , so that we get as the energy of the C-Cl bond as

$$349 - 3(\text{C-H}) = 349 - 276$$

$= 73 \text{ k cal}$ , and similarly for the others.

As can be seen from the table that Herzberg and Scheibe<sup>1</sup> got as their beginning of absorption for  $\text{CH}_3\text{Cl}$  as  $151 \text{ k cal}$ , giving a surplus of  $76 \text{ k cal}$ , over the calculated value which they could not account for. They discard any possibility of the separation of the H-Atom from the  $\text{CH}_3\text{Cl}$  molecule due to the absorption of light, as according to their calculations the limit of absorption extends towards the shorter wavelength side, and the decision arrived at was that  $\text{CH}_3\text{Cl}$  broke up into  $\text{CH}_3$  and  $\text{Cl}$  like  $\text{NaCl}$ —a process which does not account for the surplus energy. Even the excitation energy of the Halogen atom could not make up for the excess of energy. The energy states of  $\text{CH}_3$  being unknown, excitation energy of  $\text{CH}_3$  could not be added to the values.

The absorption tube used by Herzberg and Scheibe was only  $10 \text{ cms}$ . long and the pressures they used were of the order of  $1/10$  to  $1/100$  of an atmosphere. It might be said that these lengths and pressures are rather arbitrary as by no theory any hard and fast values have been provided for these. It has been found from experiments conducted in this laboratory that a length of  $100 \text{ cms}$ . with a pressure of an atmosphere gives quite a different long wave limit of continuous absorption by direct measurement, but direct measurement too does not suffice.

Other attempts are by Iredale and Wallace and Iredale and Mills. These workers also used arbitrary lengths of absorption tubes and pressures, and have found the long wave limit of absorption directly by taking the microphotogram of the plates. Iredale and mills suppose tetravalent C as in the case of  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{CH}_3\text{Cl}$  etc. exists in the  $^3\text{S}$  state. We have six electrons in C, so that we place them accordingly in the following manner in different shells

$1s$   
(2)

$2s$   
(2)

$2p$   
(2)  
 $3s$

$3p$

$3d$

If one electron is allowed to travel to (3s) we get as our normal state as  $^3P$  whereas a transfer of one electron from (2s) to (2p) shell gives us



The difference in energy between divalent C ( $^3P$ ) and ( $^5S$ ) has been calculated with the aid of some thermochemical data to be 97 k cal.

$$C(^3P) = C(^5S) - 97 \text{ k cal.}$$

in which case  $^5S$  is a deeper state. For this state, or its energy value there is yet no evidence from spectroscopic analysis. Then, the authors have calculated the value of C-H bond and from that the value of C-Br bond. But they have made use of the values 139 as heat of sublimation of C and 117 as the heat of dissociation of Oxygen-values which have been superseded by recent more correct values.\* With these values the value of the difference of  $C(^3P)$  and  $C(^5S)$  have been recalculated, and comes out to be 134 k cal. The result is that the calculated and experimental values of Iredale and Mills<sup>3</sup> are found to vary very greatly. And also in the latter case the value of one C-C bond has been lost sight of.

Mr. N. K. Saha<sup>5</sup> has calculated the value of the C-Cl bond in  $CCl_4$  on the lines of Iredale and Mills<sup>3</sup> and it has been found that the results do not tally with the more correct values of Dutta and Saha<sup>6</sup> calculated from a Born cycle.

#### EXPERIMENT

The absorption chamber was simply a tube 100 cms. in length with quartz windows, and provided with two side tubes. With one of these side tubes a glass bulb was connected in which the liquid was placed. The other was connected with a pump through a manometer. After evacuation a certain pressure of the vapour could be obtained by turning the connecting stop-cock. The source of continuous spectrum was H-tube run by a 2KW transformer, and for comparison Cu spectrum was taken in each of the plates. An E., Quartz spectrograph was used.

Microphotograms of the plates were taken by means of a Zeiss Microphotometer belonging to the Science College, Patna, and here I must thank Prof. A. T. Mukherji for his kindly allowing us to use the apparatus. My thanks are also due to Mr. M. S. Desai of this department for the trouble of taking the microphotographs for me.

The calculation and measurement of the longwave limit was done in the following manner. Along the different wavelengths for each of the plates, the ratio of the intensities of the continuous and absorption spectrum at certain pressure, with the intensity of the continuous as 100 was calculated and plotted with wavelength as abscissa. The curves were found to touch the abscissa at one wavelength for each substance giving the beginning of absorption. For example

in the case of  $\text{CH}_3\text{Cl}$ , a visual observation of the limit as 2100 was extended to 2200 from the curves.

It might be supposed that the primary act of light is to break the C-Cl bond requiring the energy corresponding to 2200, *i.e.*, 130 k cal. Other substances tried were  $\text{C}_2\text{H}_5\text{Cl}$ , normal  $\text{C}_3\text{H}_7\text{Cl}$ , and normal  $\text{C}_4\text{H}_9\text{Cl}$ , but in all these cases no perceptible differences were found for the value of the C-Cl bond.

In conclusion I wish to express my thanks to Prof. M. N. Saha, for his kind interest and guidance during the course of the work.

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- <sup>1</sup> Herzberg and Scheibe, *Zeit. Physikal. Chem.* 7, B. 390, 1930.
- <sup>2</sup> Iredale and Wallace, *Phil. Mag.* 8, 1093, 1929.
- <sup>3</sup> Iredale and Mills, *Proc. Roy. Soc. A* 133, 430, 1931.
- <sup>4</sup> A. K. Dutta, *Proc. Roy. Soc. A* 137, 366, 1932.
- <sup>5</sup> N. K. Saha, *Absorption Spectra of Some Halogen Derivation of Methane* (to be published in these Bulletins).
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# ON THE DETERMINATION OF THE VAPOUR PRESSURES OF ZINC BROMIDE

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## INTRODUCTION

*'Vapour pressure determinations are of great practical value, not least for the molecular ray technique itself but undoubtedly the most important use to be made at the present time of accurate vapour pressure data is in establishing the validity of certain very interesting points in the theory of thermodynamics'* (Molecular Rays by Ronald G. J. Fraser, p. 176). We may add that it is also necessary for testing the modern theories of chemical binding.

The knowledge of the vapour pressures of solids enables us to determine the latent heat of evaporation of the substance. In the present case the latent heat of zinc bromide was required to test the new theory of continuous absorption of halides of divalent atoms, such as zinc.

The theory of absorption of the halides of monovalent elements has been satisfactorily given by Born and Franck,<sup>1</sup> but very little work has been done on the halides of the poly-atomic elements. Attempt has been made by Dutta and Saha<sup>2</sup> to put forward a theory of absorption of the halides of multivalent elements, but the theory yet requires more definite confirmation from experimental results.

In the case of the halides of monovalent elements, if  $\lambda$  be the beginning of absorption on the longer wavelength side,  $h\nu$  exactly corresponds to the value,

$$R = \frac{N h \nu}{J} = \frac{286000}{\lambda} \quad \dots \quad \dots \quad (1)$$

$$\text{or } \lambda = \frac{286000}{R}$$

and

$$R = Q + \frac{1}{2} D_{x_2} + L_M - L_{MX}$$

The theory, in its present state says that in the case of the halides of multi-valent elements  $MX_n$  the beginning of absorption  $\lambda$  can be expressed as

$$\lambda = 286000 \times \frac{n}{R} \quad \dots \quad \dots \quad (2)$$

In the case of halides of di-valent elements  $n=2$  and

$$R = Q + D_{x_2} + L_M - L_{MX_2}$$

The purpose of the present work is to determine the latent heat of  $ZnBr_2$  in order that equation (2) may be accurately tested.

#### METHOD

The method used is that of effusion of vapour through a small hole, at an extremely low pressure, when heated at a constant temperature, for a definite time. The method was first suggested by Knudsen and largely used by Egerton, Harteck and others.\* From the kinetic theory of gases we obtain the relation,

$$p = \frac{m}{A t} \sqrt{\frac{2 R T}{M}} \quad \dots \quad \dots \quad (3)$$

Where  $p$  is the vapour pressure at  $T^\circ K$ ,  $m$  is the mass of the effused vapour,  $t$  is the duration of effusion in seconds,  $A$  is the area of the hole,  $M$  is the molecular weight of the substance, and  $R=8.3 \times 10^7$ . It must be noted that the above relation holds good only when the temperature is such that the molecules neither dissociate nor associate.

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\* See note at the end of the paper.

## EXPERIMENT

The apparatus used is shown in Figure 1.

*The apparatus.*—The vapour pressure apparatus of transparent quartz was made according to our design as in the figure. It was kept inside an electrical

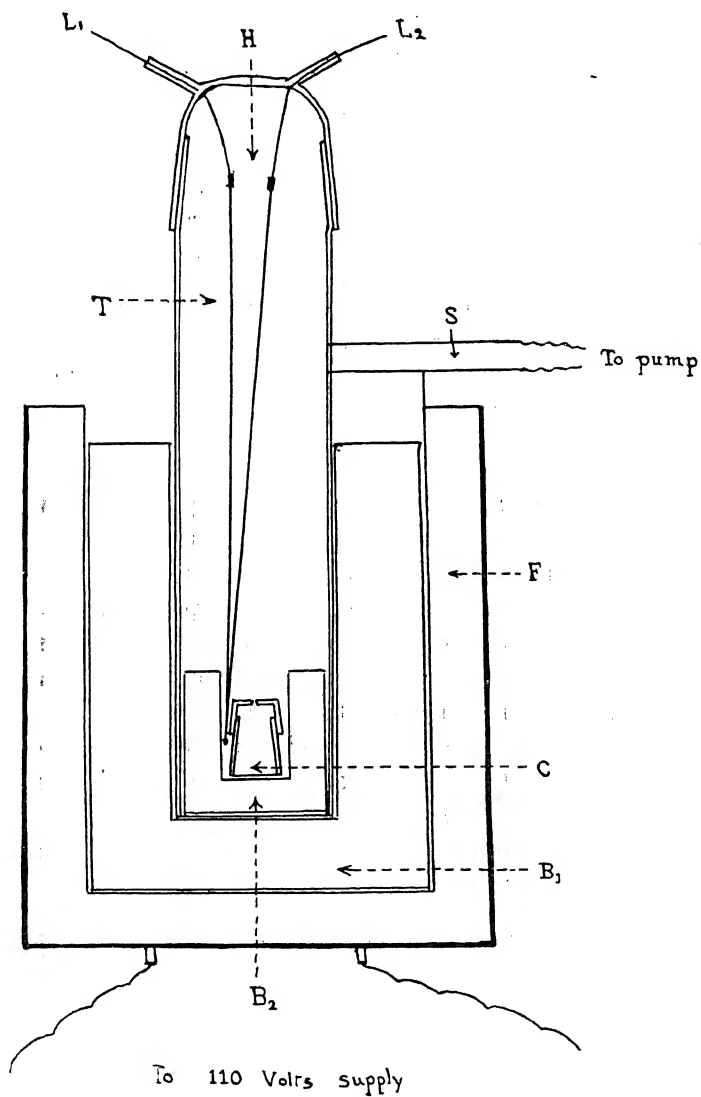


Fig. 1

furnace  $F$ , within a hole cut in the brass block  $B_1$  (which when heated ensures uniformity of temperature,

Anhydrous zinc bromide supplied by Merck was weighed and kept inside a quartz crucible C, having a fine hole in the lid. The crucible was put inside a cylindrical thick copper block B<sub>2</sub> and introduced inside the apparatus. The junction of a copper-constantine thermocouple was introduced inside the copper block B<sub>2</sub>, by the side of the crucible. The thermojunction was put inside quartz tubing and protected from the effects of the vapour inside the apparatus.

The quartz apparatus consists of mainly three parts: the main tube T, the ground head H, and the crucible C. (i) The main tube T is about 40 cms. long and has a diameter of 4 cms. The wall is about 1.5 mms. thick. The bottom is flat and the mouth conical in shape, and ground accurately. It has a side tube S for the connection to the high vacuum pump. (ii) The head H is conical and also accurately ground to fit vacuum tight on the tube T. It has two thermocouple leads L<sub>1</sub> and L<sub>2</sub> at the top. (iii) The crucible is also conical of about 2 cms. height having a ground cover with a fine hole in the centre of the cover.

*The Furnace.*—Uniformity of temperature is attained by means of two metallic blocks B<sub>1</sub> and B<sub>2</sub>. The furnace was heated electrically from a 110 volts D. C. supply. The current was kept constant by adjusting the resistance with the aid of a very fine rheostat. The maximum current which the furnace could bear was 5 amps.

*Vacuum.*—Special care was taken to attain very high vacuum. A 3-stage mercury diffusion pump was used as the primary pump and a Max Kohl's oil pump was used as secondary pump. Before connecting the main apparatus, the available vacuum was tested by means of a discharge tube, and the conditions were so perfect that no discharge stage was soon obtained, and the vacuum could balance a spark gap of about 5 to 6 inches. In order to avoid the mercury vapour from diffusing into the main apparatus the conical end of the pump was surmounted by an accurately fitting steel tube 24 inches long, which was surrounded by a jacket. The jacket was filled with ordinary freezing mixture. This ensures a vacuum of very high order of about  $10^{-6}$  mms. and prevents diffusion of mercury completely, as is shown by the fact that no mercury lines are observed when discharge is passed through the discharge tube.

*Temperature.*—The temperature was measured by means of a well prepared copper-constantine thermocouple. The junctions of the thermocouple were welded electrically in a carbon arc. The colder junction was kept at zero degree (in melting ice), and the thermal voltage was read by means of an accurate millivoltmeter reading up to 0.5 mv. Special care was taken to avoid the effect of the vapour on the thermojunction by protecting it inside a quartz tube. The inner junction was introduced inside as near the crucible as possible. The thermocouple was first calibrated by putting it inside fixed temperature baths. It gave values almost identical with those given by Landolt and Börnstein.\* The temperatures at which

the experiment was carried out was below the temperature of dissociation of zinc bromide.

*Time*—Time was counted by means of a chronometer reading accurately up to half a second, which was quite sufficient for the purpose. In order to start counting just when the experiment began, and stop counting when the experiment stopped, the following procedure was adopted. The substance was introduced inside and the apparatus evacuated. After perfect evacuation a small pressure of nitrogen was introduced inside the heated furnace. As long as the furnace contains some gas no effusion takes place. When the thermocouple shows a constant reading the nitrogen was pumped out, the counting was commenced just when soft X-ray stage was reached. Before stopping the experiment, nitrogen was introduced in the same way.

*Area*.—The area of the hole is a very important determination and requires great accuracy in its measurement. The following method was devised for the accurate measurement. The top surface of the lid of the crucible was projected on a sheet of graph paper by the help of a very powerful epidiascope. A fine scale, accurately graduated in half millimeters, was also placed by the side of the hole. This was meant for the determination of the linear magnification. The inner border of the image of the hole was traced on the squared paper, and the area was determined by counting the number of the squares covered by the image of the hole. The true area was obtained by dividing the area so obtained by the square of the linear magnification. Different magnifications were used by changing the distance of the screen and the average value of  $A$  was determined.

*Mass*.—The mass of the vapour effusing out was measured by the method of differences. The empty crucible was repeatedly heated in vacuum till it gave a constant weight. The salt was put inside and weighed before the experiment was commenced and again at the end of the experiment. The loss of weight gives us the mass which has effused out. A very fine chemical balance was used for weighing

## RESULTS

In equation (3) the constant quantities are,  $M$  the molecular weight of zinc bromide = 225.2. The area of the hole is 0.0263 square cms. The other quantities are given in the following Table 1.



Table 1.

| Mass in gms.<br>m | Time of heating<br>T sec. | Thermo-volt<br>M. V. | Temp °C. | P (mm.) calculated |
|-------------------|---------------------------|----------------------|----------|--------------------|
| ·1368             | 1500                      | 13·0                 | 208      | ·0933              |
| ·0673             | 1260                      | 14·1                 | 316      | ·1382              |
| ·2960             | 1200                      | 16·6                 | 346      | ·2669              |
| ·7423             | 1800                      | 17·5                 | 360      | ·4211              |
| ·5126             | 900                       | 18·2                 | 374      | ·6832              |
| ·8264             | 900                       | 19·0                 | 389      | 1·0280             |
| ·9472             | 720                       | 19·8                 | 400      | 1·6090             |

## THE VAPOUR PRESSURE EQUATION

The results which have been obtained could be expressed in the form of an equation similar to one given by Knudsen<sup>5</sup> for mercury.

Starting from the Clausius' equation we get

$$\lambda = R T^2 \frac{d \ln p}{dT}$$

and  $\lambda = \lambda_0 - (C - C_p) T$ , where  $C$  is the molecular heat of the vapour at constant pressure, whence

$$\ln p = -\frac{\lambda_0}{RT} - \frac{(C - C_p)}{R} \log T + k$$

but assuming

$$C - C_p = 3R - \frac{5}{2}R = \frac{R}{2}$$

$$p = k \cdot T^{-\frac{1}{2}} \cdot e^{-\lambda_0/RT}$$

This gives

$$\log_e p = -\frac{\lambda_0}{RT} - \frac{1}{2} \log_e T + \log_e k$$

$$\log_{10} p = -\frac{\lambda_0}{2.3 RT} - 0.5 \log_{10} T + k' \quad \dots \quad (4)$$

This is of the form,

$$\log p = -\frac{A}{T} - 0.5 \log T + B$$

Table 2 gives the values of  $\log p$  and  $\log T$  and graph I shows the actual graph between  $\log p$  and  $\log T$ .

Table 2.

| Temp °C | Temp °K | $\log_{10} T$ | Press. mms. | $\log_{10} P$ |
|---------|---------|---------------|-------------|---------------|
| 280     | 553     | 2.7427        | 0.0933      | -1.0302       |
| 316     | 589     | 2.7701        | 0.1382      | -0.8595       |
| 346     | 619     | 2.7917        | 0.2669      | -0.5736       |
| 360     | 633     | 2.8014        | 0.4211      | -0.3756       |
| 374     | 647     | 2.8109        | 0.6832      | -0.1658       |
| 389     | 662     | 2.8209        | 1.0280      | 0.0342        |
| 400     | 673     | 2.8280        | 1.6090      | 0.2063        |

Further we have the equation,

$$\log p = -\frac{A}{T} - 0.5 \log T + B$$

Where  $A = \frac{\lambda_0}{2.3R} \quad \dots \quad \dots \quad \dots \quad (5)$

Now from our experimental data we shall evaluate the constants of the equations, *viz.*, A and B. We have,

| T°A | $\log T$ | $\log P$ |
|-----|----------|----------|
| 633 | 2.8014   | -0.3756  |
| 662 | 2.8209   | 0.0342   |

Substituting this data and solving the equations we get,

$$A = 6063.0$$

and  $B = 10.6041$

Thus the vapour pressure equation for zinc bromide, between the temperatures 300°C to 400°C is

$$\log p = \frac{-6063}{T} - 0.5 \log T + 10.6041 \quad \dots \quad \dots \quad (6)$$

## THE LATENT HEAT OF EVAPORATION

From the equation (5) we have

$$A = \frac{\lambda_0}{2.3 R}$$

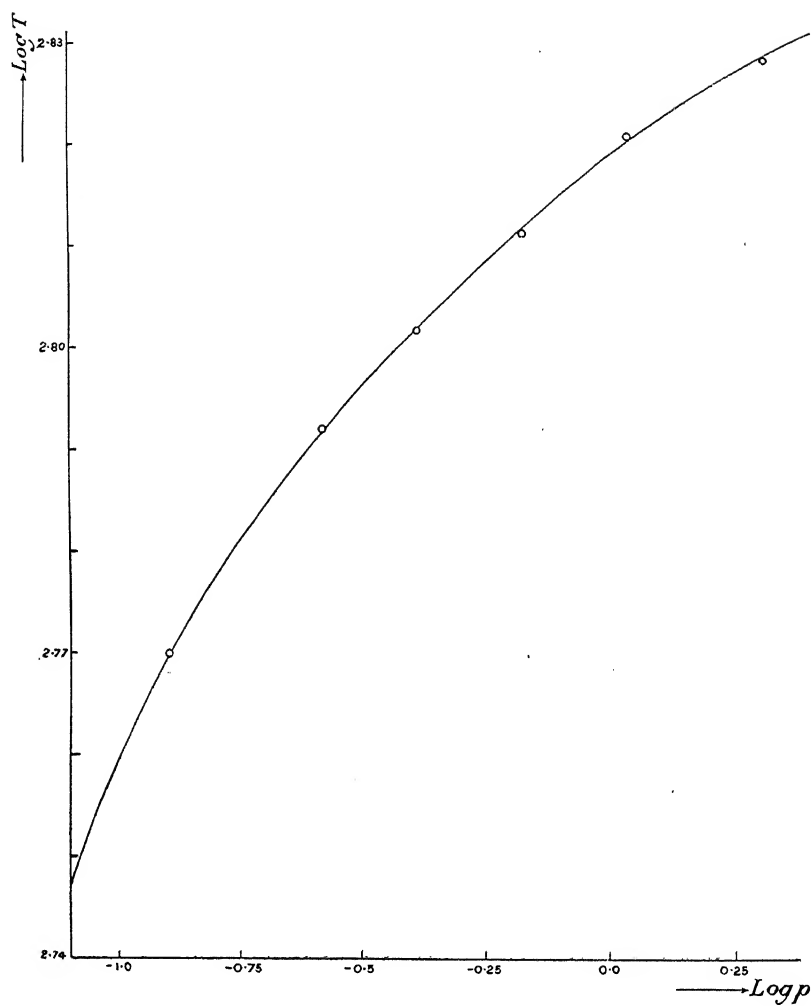


Fig. 2

$\therefore$  Latent heat  $\lambda_0 = 4.554 A$

$= 27600$  calories

or  $= 27.6$  k. cal.

## SUMMARY

In the present paper the vapour pressures of Zn Br<sub>2</sub> (anhydrous) are determined over the range of temperatures from 280°C to 400°C by the method of effusion of the vapour from a small hole the values obtained are

| T°C. | p (mm.) |         |
|------|---------|---------|
| 280  | 0.933   |         |
| 316  | 1.382   |         |
| 346  | 2.669   |         |
| 360  | 4.211   | ... (I) |
| 374  | 6.832   |         |
| 389  | 10.280  |         |
| 400  | 16.090  |         |

The graph drawn between the values of log *p* and log *T* shows curve according to the equation

$$\log p = - \frac{A}{T} - 0.5 \log T + B$$

where  $A = \frac{\lambda_0}{2.3 R}$

The constants A and B are determined by making use of the experimental data and the equation is evaluated to be,

$$\log_{10} p(\text{mm}) = - \frac{6063}{T} - 0.5 \log_{10} T + 10.6041 \quad \dots \quad \dots \quad \text{(II)}$$

Further from the value of A ( = 6063 ) the latent heat of evaporation of zinc bromide is evaluated to be,

$$L = 27.60 \text{ k. cal.} \quad \dots \quad \dots \quad \dots \quad \dots \quad \text{(III)}$$

## ACKNOWLEDGEMENT

My sincere thanks are due to Prof. M. N. Saha, for his valuable guidance and interest throughout the work.

*Note.*--Substances whose vapour pressures have been determined by the effusion method, so far as they are known to me, are the following :

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Na—Rodebush and de Uries, *J. Amer. Chem. Soc.*, **47**, 2488, 1925.

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K—Edmundson and Egerton, *Loc. Cit.*

Cu—Harteck, *Zeits-Physikal. Chem.* **134**, 1, 1928.

Ag—Harteck }  
Au—Harteck } *Loc. Cit.*

Zn }  
Cd } —Egerton, *Phil Mag.* **33**, 33, 1917.

Hg—Knudsen *Ann der Physik* **29**, 179, 1909.

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Ca—Harteck *Loc. Cit.*

Sn—Harteck *Loc. Cit.*

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<sup>3</sup> Knudsen, *Ann der Physik* **29**, 179, 1909.

<sup>4</sup> Landolt and Börnstein tables, *3rd Ed.*, Berlin, 1923, p. 1029.

# AN X-RAY INVESTIGATION OF THE CRYSTALS OF DIPHENYL NITROSOAMINE.

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Diphenyl nitrosoamine was crystallised from a mixture of alcohol and benzene. The crystals have been examined crystallographically and have been found to develop  $c$  (001) and  $m$  (110) faces.  $q$  (011) and  $o$  (101) also appear but not in a well developed form. The crystals belong to the monoclinic prismatic class and the axial ratio is<sup>1</sup>

$$\begin{aligned} a : b : c &= 0.9635 : 1 : 1.5637 \\ \beta &= 90^\circ 58' \end{aligned}$$

The crystals were examined by the rotating crystal method. The rotation photographs were taken by means of Shearer X-ray tube fitted with copper anticathode: those obtained about  $a$  and  $b$  axes are shown in figures 1 and 2 (plate I). The lengths of the axes were determined from

$$l = \frac{n\lambda}{2z} \sqrt{(2r)^2 + (2D)^2}$$

where  $l$  = the length of the axis,

$n$  = the order of the hyperbola,

$\lambda$  = the wavelength of the incident X-rays,

$z$  = the distance of a spot from the zero line,

$r$  = the distance of the spot from the centre,

$D$  = the distance of the plate from the crystal.

The mean values of  $a$ ,  $b$  and  $c$  were thus found to be

$$a = 17.08 \text{ \AA}; \quad b = 8.8675 \text{ \AA}; \quad c = 28.07 \text{ \AA}.$$

The axial ratio is

$$a : b : c = 1.926 : 1 : 3.166$$

The value of  $\beta$  was assumed to be  $90^\circ 58'$ , the same as the value given by Groth. It can be seen from the above that the ratios of  $a$  &  $b$  and of  $c$  &  $b$  are exactly twice of that found by the crystallographic measurements.

Oscillation photographs about the  $a$  and  $b$  axes were taken at an interval of  $15^\circ$  and the indices of the reflecting planes corresponding to the spots on the oscillation photographs were worked out by Bernal's method of analysis.<sup>2</sup>

The planes observed, together with an approximate idea of their relative intensities, are given in tables 1 and 2. The method adopted in estimating the intensity of the spot was that used by Robertson.<sup>3</sup> The symbols used have the following meaning:

v. s. = very strong      m = medium  
 s. = strong      w. m. = weak medium  
 m. s. = medium strong      w = weak  
 v. w. = very weak.

Table 1

| Axial Planes | (hol) Planes | (ho $\bar{l}$ ) Planes | (okl) Planes | (hko) Planes |
|--------------|--------------|------------------------|--------------|--------------|
| 004 v. s.    | 202 m. s.    | 20 $\bar{2}$ m. s.     | 012 s.       | 210 v. s.    |
| 008 s.       | 206 v. s.    | 20 $\bar{6}$ v. s.     | 016 v. s.    | 230 s.       |
| 0012 v. w.   | 2010 m.      | 20 $\bar{1}0$ m.       | 0110 m.      | 420 m.       |
| 020 v. s.    | 2014 m. s.   | 20 $\bar{1}4$ m.       | 0114 w. m.   | 610 w. m.    |
| 400 v. s.    | 404 s.       | 40 $\bar{4}$ s.        | 024 s.       | 620 v. w.    |
| 600 w.       | 406 v. w.    | ...                    | 028 s.       | 820 w.       |
| 800 w.       | 408 w. m.    | ...                    | 0212 w. m.   |              |
|              | ...          | 60 $\bar{2}$ m.        | 0214 m. s.   |              |
|              | ...          | 60 $\bar{4}$ m.        | 032 s.       |              |
|              | 606 s.       | 60 $\bar{6}$ w.        | 036 m. s.    |              |
|              | 6010 m. s.   | 60 $\bar{1}0$ w. m.    | 0310 m. s.   |              |
|              | 802 w.       | ...                    | 048 m.       |              |
|              | 804 w. m.    | 80 $\bar{4}$ w.        |              |              |
|              | ...          | 80 $\bar{6}$ w.        |              |              |

Table 2.—General Planes.

|      |       |               |       |      |       |               |       |              |       |               |       |
|------|-------|---------------|-------|------|-------|---------------|-------|--------------|-------|---------------|-------|
| 111  | s.    | 11 $\bar{1}$  | s.    | 214  | s.    | 21 $\bar{4}$  | s.    | 311          | w.    | 31 $\bar{1}$  | m.    |
| 113  | s.    | ...           |       | 218  | m.    | 21 $\bar{8}$  | m.    | 313          | v. s. | 31 $\bar{3}$  | v. s. |
| 115  | v. s. | 11 $\bar{5}$  | v. s. | ...  |       | 21 $\bar{10}$ | m. s. | 31 $\bar{5}$ | v. s. | 31 $\bar{5}$  | s.    |
| 119  | m. s. | 11 $\bar{9}$  | m. s. | 2112 | w.    | 21 $\bar{12}$ | v. w. | 317          | m. s. | ...           |       |
| 1113 | w.    | 111 $\bar{3}$ | v. w. | 222  | s.    | 22 $\bar{2}$  | s.    | 319          | m. s. | 31 $\bar{9}$  | v. w. |
| 1115 | w.    | 111 $\bar{5}$ | v. w. | 226  | s.    | 22 $\bar{6}$  | s.    | 3111         | w. m. | 311 $\bar{1}$ | v. w. |
| 121  | v. s. | 121           | v. s. | ...  |       | 22 $\bar{8}$  | m. s. | 3113         | m.    | ...           |       |
| 125  | s.    | 12 $\bar{5}$  | v. s. | 2210 | m. s. | 22 $\bar{10}$ | m. s. | 321          | v. s. | ...           |       |
| 127  | m. s. | ...           |       | 2214 | w. m. | ...           |       | ...          |       | 32 $\bar{3}$  | v. w. |
| 129  | m. s. | 12 $\bar{9}$  | m. s. | 232  | m. s. | 23 $\bar{2}$  | w. m. | 325          | m. s. | 32 $\bar{5}$  | s.    |
| 131  | s.    | ...           |       | 234  | m.    | 23 $\bar{4}$  | m. s. | 327          | w. m. | 32 $\bar{7}$  | w. m. |
| 133  | v. w. | 13 $\bar{3}$  | w. m. | ...  |       | 23 $\bar{6}$  | v. w. | 3213         | m.    | ...           |       |
| 135  | m.    | 13 $\bar{5}$  | m.    | 238  | w. m. | 23 $\bar{8}$  | w. m. | 331          | m.    | 33 $\bar{1}$  | m.    |
| ..   |       | 13 $\bar{7}$  | m.    | ...  |       | 23 $\bar{10}$ | m.    | 333          | w.    | 33 $\bar{3}$  | v. w. |
| 139  | m.    | 13 $\bar{9}$  | w. m. | 242  | w. m. | ...           |       | 337          | m. s. | 33 $\bar{7}$  | m. s. |
| 141  | w. m. | ...           |       | ...  |       | 24 $\bar{4}$  | w. m. | ...          |       | 34 $\bar{3}$  | w.    |
| 143  | w. m. | ...           |       | 246  | w. m. | 24 $\bar{6}$  | m.    | 345          | w. m. | 34 $\bar{5}$  | m.    |
| 145  | m. s. | 14 $\bar{5}$  | m. s. |      |       |               |       |              |       |               |       |
| 147  | w.    | 14 $\bar{7}$  | m.    |      |       |               |       |              |       |               |       |
| 412  | m. s. | 41 $\bar{2}$  | s.    | 511  | m. s. | 51 $\bar{1}$  | s.    | 612          | m. s. | 61 $\bar{2}$  | v. w. |
| 416  | w.    | 41 $\bar{6}$  | w. m. | 513  | v. s. | 51 $\bar{3}$  | v. s. | 614          | w. m. | 61 $\bar{4}$  | w.    |
| 418  | v. w. | 41 $\bar{8}$  |       | 515  | w.    | 51 $\bar{5}$  | w.    | ...          |       | 61 $\bar{6}$  | m. s. |



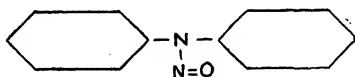
Table 2 (continued)

|      |       |      |       |      |       |      |       |       |       |       |       |
|------|-------|------|-------|------|-------|------|-------|-------|-------|-------|-------|
| 4110 | m. s. | ...  | 517   | s.   | 517   | m.   | 618   | m. s. | 618   | m. s. |       |
| ...  |       | 4114 | w.    | 519  | m.    | 519  | v. w. | 6112  | m. s. | ...   |       |
| 424  | m.    | 424  | w. m. | 521  | s.    | 521  | s.    | 622   | w. m. | 622   | m. s. |
| 428  | v. w. | 428  | m. s. | ...  |       | 523  | m. s. | 626   | w. m. | 626   | m.    |
| 4212 | w. m. | 4212 | v. w. | 525  | m. s. | 525  | m. s. | 628   | w. m. | 628   | m.    |
| 432  | w. m. | ...  |       | 527  | m.    | 527  | m.    | 6210  | w.    | 6210  | v. w. |
| ...  |       | 434  | m. s. | ...  |       | 529  | v. w. | 632   | v. w. | 632   | m.    |
| ...  |       | 436  | m.    | 5211 | w.    | 5211 | v. w. | 634   | v. w. | 634   | v. w. |
| 438  | m. s. | ...  |       | 5213 | v. w. | ...  |       | 638   | w.    | ...   |       |
| 4310 | v. w. | 4310 | v. m. | 535  | w.    | 535  | w.    | ...   |       | 6310  | w.    |
| 444  | m.    | 444  | w. m. | ...  |       | 533  | w. m. | ...   |       | 642   | v. w. |
| ...  |       | 448  | w.    | 537  | m. s. | 537  | m. s. | ..    |       | 646   | m.    |
|      |       |      |       | 539  | w. m. | 539  | w.    |       |       |       |       |
|      |       |      |       | 5311 | w.    | 5311 | v. w. |       |       |       |       |
|      |       | 711  | w. m. | ...  |       | 812  | m. s. | ...   |       |       |       |
|      |       | 713  | m. s. | 713  | m.    | 816  | w.    | ..    |       |       |       |
|      |       | 715  | w.    | ...  |       | ...  |       | 824   | w. m. |       |       |
|      |       | 717  | w.    | 717  | w.    |      |       |       |       |       |       |
|      |       | ...  |       | 719  | w.    |      |       |       |       |       |       |
|      |       | 723  | v. w. | 723  | m.    |      |       |       |       |       |       |
|      |       | 725  | m. s. | 725  | w.    |      |       |       |       |       |       |
|      |       | 731  | m. s. | ...  |       |      |       |       |       |       |       |
|      |       | 733  | v. w. | ...  |       |      |       |       |       |       |       |

It will be seen from the above list that the planes (001) are quartered and (100) and (010) are halved and (hkl) planes are halved when (h+1) is odd. These halvings correspond to the space group  $C_{2h}^3$  with  $\overline{m}'$  Bravais Lattice.\*

The number of molecules in the unit cell required by the space group  $C_{2h}$  is sixteen. The number of molecules in the unit cell calculated from the dimensions of the cell and the specific gravity of the crystals which was found to be 1.251, also comes out to be nearly sixteen. This indicates that the molecules of diphenyl nitrosoamine in the cell are asymmetric.

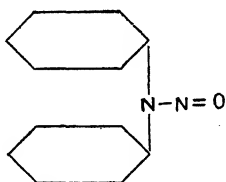
The chemical structure of diphenyl nitrosoamine is represented as



If the benzene rings are assumed to be plane rings of carbon atoms having diameter 1.42 Å and the centres of the carbon atoms and that of the nitrogen atom lie on the same line, the length of the molecule comes out to be nearly 12 Å.

It will be seen from the list of the planes that (hkl) and  $(h\bar{k}l)$  have in the majority of cases nearly the same intensity. The unit cell, therefore, behaves like an orthogonal cell: this, however, is expected as the angle  $\beta$  is nearly 90°.

From the quartering of the (001) planes it appears that the molecules of diphenyl nitrosoamine in the unit cell lie with their length parallel to the  $c$  axis. But as the length provided for the purpose is only about 7 Å, it appears that the molecules in the cell are situated not in the manner indicated above but probably as

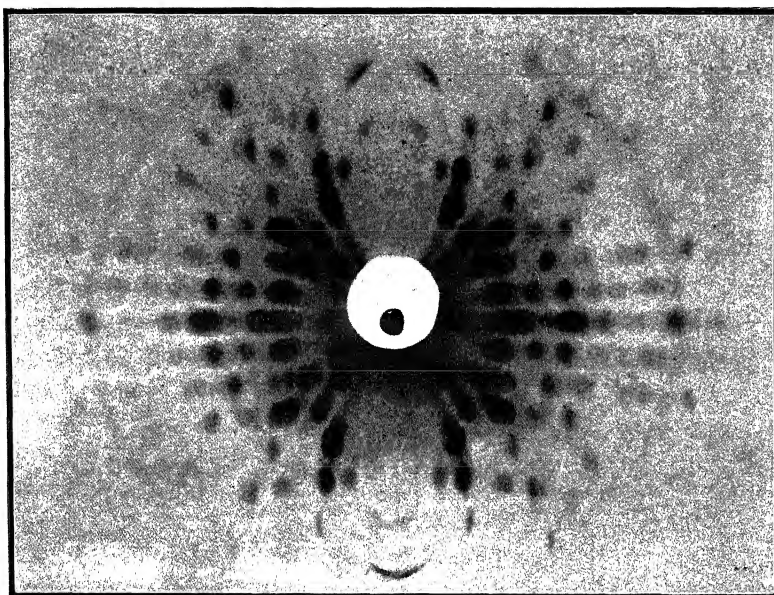


The considerations of the dimensions of this arrangement of the rings and those of the unit cell further indicate that the two rings are situated nearer to the  $ac$  face than to the  $bc$  face and they are slightly inclined to each other and to the  $ac$  face. The oxygen atom is probably situated along the direction of the  $b$  axis. This arrangement of two rings is different from the one which has been observed

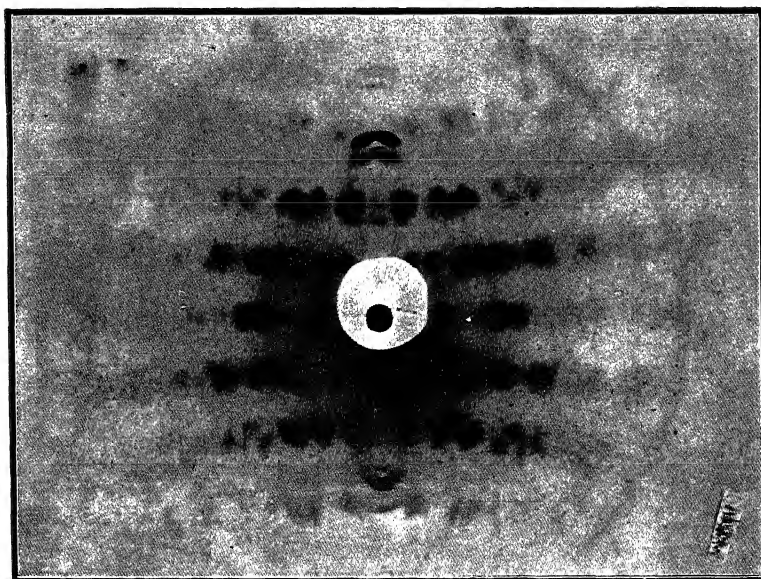
in the unit cells of diphenyl or other substances of similar structure studied in this laboratory.

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Rotation Photograph about the  $a$ -axis



Rotation Photograph about the  $b$ -axis

# VISCOSITY OF FERRIC PHOSPHATE SOL AT VARIOUS PRESSURES

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In several publications Dhar and coworkers<sup>1</sup> have shown that the viscosity of sols goes on increasing with dialysis and finally the sol becomes very viscous and has a tendency to set to a jelly. We have shown<sup>2</sup> in the case of such sols as those of gelatine, agar, etc., that there exists a definite labile structure of the colloid particles, which can suitably explain their high viscosity.

Moreover, in recent years a large amount of work is accumulating on the measurement of viscosity of colloids and it has been found that there exists a great anomaly in this physical property of colloids. Thus Hess<sup>3</sup> showed with blood sols, Hatschek<sup>4</sup> with gelatine sols, Herschel and Bulkley<sup>5</sup> with rubber sols, Ostwald and coworkers<sup>6</sup> with gelatine and mercury sulphosalicylate sols that the viscosity coefficients differed with the change in the shearing force causing the flow of the sols. In fact they observed that the so-called viscosity remarkably decreases as the force of shear is increased. Similarly, Freundlich and coworkers<sup>7</sup> have shown with some inorganic colloids like those of ferric hydroxide (aged) and vanadium pentoxide, that the simple law of Poiseuille, *viz.*, that the rate of flow is directly proportional to the shearing force, is not applicable in such cases. In view of these facts we have studied the viscosity of ferric phosphate sol of various degree of purity at various stages of dialysis under variable pressures. Ferric phosphate sol is well known to form viscous sols and yield gels. The viscosity of the sol at various pressures is measured with the apparatus designed by Hoskings<sup>8</sup> to measuring the viscosity of liquids. In order to control the pressure changes during the flow. An empty vessel of 8 to 10 litres capacity was introduced between the manometer and the apparatus.

Ferric phosphate sol was prepared by adding  $\text{KH}_2\text{PO}_4$  solution to a fairly concentrated  $\text{FeCl}_3$  solution in small amounts at the room temperature till the sol formed assumes a pale yellow colour. The sol of ferric phosphate thus obtained contains an excess of  $\text{FeCl}_3$ , and  $\text{HCl}$  and  $\text{KCl}$  obtained by the reaction. The sol was kept in a parchment paper for dialysis and as the dialysis progressed the sol was gradually freed from the impurities and thus we obtained the sols of ferric phosphate of various degrees of purity. The purity of the sol was determined from

the estimation of chloride ions present in the sol. The viscosity measurements were carried on at 22°C.

Table 1.

Sol dialysed for 4 days.

Strength of the sol = 21.36 grams of ferric phosphate per litre (Sol A).

| (Sol A) | Pressure           | S (sol)/ $\eta_w$ |
|---------|--------------------|-------------------|
|         | Cms. water column. |                   |
|         | 19.8               | 1.146             |
|         | 30.0               | 1.098             |
|         | 40.0               | 1.093             |
|         | 50.2               | 1.089             |
|         | 60.0               | 1.085             |
|         | 70.5               | 1.083             |

Table 2.

Sol dialysed for 6 days.

Strength of the sol = 20.82 grms. ferric phosphate per litre (Sol A).

| Pressure           | Sol A           | Sol A/2           | Sol A/4           |
|--------------------|-----------------|-------------------|-------------------|
| Cms. water column. | S (sol)/ $\eta$ | S (sol)/ $\eta_w$ | S (sol)/ $\eta_w$ |
| 19.8               | 1.368           | 1.136             | 1.070             |
| 30.0               | 1.277           | 1.095             | 1.048             |
| 40.0               | 1.237           | 1.092             | 1.046             |
| 50.2               | 1.224           | 1.089             | 1.042             |
| 60.0               | 1.218           | 1.085             | 1.040             |
| 70.5               | 1.213           | 1.083             | 1.040             |

Table 3.

Sol dialysed for 8 days.

Strength of the sol = 19.64 grms. ferric phosphate per litre (Sol A).

| Pressure          | Sol A             | Sol A/2           | Sol A/4           |
|-------------------|-------------------|-------------------|-------------------|
| Cms. water column | S (sol)/ $\eta_w$ | S (sol)/ $\eta_w$ | S (sol)/ $\eta_w$ |
| 19.8              | 1.545             | 1.282             | 1.155             |
| 30.0              | 1.513             | 1.272             | 1.138             |
| 40.0              | 1.500             | 1.265             | 1.135             |
| 50.2              | 1.494             | 1.260             | 1.131             |
| 60.0              | 1.488             | 1.258             | 1.127             |
| 70.5              | 1.485             | 1.256             | 1.127             |

Table 4.

Sol dialysed for 10 days.

Strength of the sol = 19.0 grms. ferric phosphate per litre (Sol A).

| Pressure<br>Cms. water column | Sol A<br>$S(\text{sol})/\eta_w$ | Sol A/2<br>$S(\text{sol})/\eta_w$ | Sol A/4<br>$S(\text{sol})/\eta_w$ |
|-------------------------------|---------------------------------|-----------------------------------|-----------------------------------|
| 19.8                          | 3.545                           | 1.997                             | 1.395                             |
| 30.0                          | 3.489                           | 1.908                             | 1.362                             |
| 40.0                          | 3.415                           | 1.890                             | 1.346                             |
| 50.2                          | 3.373                           | 1.876                             | 1.325                             |
| 60.0                          | 3.333                           | 1.865                             | 1.304                             |
| 70.5                          | 3.250                           | 1.855                             | 1.300                             |

From our experimental results we find that with the progress of dialysis the sol becomes unstable and the viscosity  $s$  increases rapidly with purity, *e.g.*, as the impurities possessing the stabilising effect on the sol are removed the sol becomes unstable and viscous. Similar results have been obtained by Dhar and coworkers with other sols. Our results, however, show that the increase in the viscosity  $s$  of ferric phosphate sol of various grades of purity is less marked when the flow is caused by high pressures. Similarly, in the case of diluted sols, the increase in the value of  $s$  with the progress of dialysis is not so marked as in the case of concentrated ones.

We are, therefore, of opinion that a high rise in the viscosity of sols as is generally observed during the process of dialysis and measured by an Ostwald's viscometer is certainly due to the fact that the pressure causing the flow of a colloid in an Ostwald's viscometer is very low. It appears to us that if the measurements of the rates of flow of a colloid be undertaken at fairly high pressures (this may not be experimentally possible because of turbulent flow) the change in the viscosity of colloids when it is purified be either nil or insignificant.

It is also seen from our results that the value of  $s$  increases more rapidly with the increasing concentration of the dispersing medium than that demanded by any linear relationship and a sol of ferric phosphate behaves like some typical hydrophilic colloids as those of gelatine, agar, starch, etc. It may be mentioned here that simple equation connecting the concentration of a colloid with its viscosity was first given by Einstein,<sup>9</sup> *viz.*,  $\eta_s = \eta (1 + a\phi)$ , where  $\eta_s$  and  $\eta_w$  represent the viscosities of the sol and water respectively,  $a$  is a constant and  $\phi$  is the ratio of the total volume of the dispersed phase to the volume of the sol. From time to time this equation has been put to experimental test and has been found to be not applicable specially in the case of lyophilic colloids. Several other relations have been proposed by Hess,<sup>10</sup> Hatschek,<sup>11</sup> Arrhenius<sup>12</sup> and others to correlate the viscosity of a sol with the concentration of the dispersed phase. Our experimental results show that as the pressure causing the flow of a sol of ferric phosphate

increases the curves connecting viscosity with the concentration of ferric phosphate gradually flatten out to assume the form of a straight line. We think, therefore, that in view of the fact that there is a wide variation of viscosity and that of a tendency for the change in the nature of the concentration viscosity curves with the rate of shear, it is not profitable to use the formula of Hess, Hatschek, Arrhenius and others and to calculate the degree of hydration therefrom.

It is generally believed by colloid chemists that a high viscosity of sol is due to a high hydration of colloid particles. According to this view we have to explain our experimental results on the assumption that the hydration of the colloid particles is changeable by the shearing force, which causes the flow of the sol through a capillary; moreover, we have to assume that the hydration of the colloid particles increase with diminution in their electrical charge.

From our results it is seen that the percentage increase of viscosity at lower rates of shear is highly magnified with the greater purity of sols. In some cases a pure sol has a viscosity 2.5 to 3 times that of a sol which is comparatively impure. This will lead us to assume that a large increment in hydration occurs as the electric charge on the colloid particle is diminished. This increased hydration will then cause the effective volume of the colloid particle to become very large and we are to assume that the adsorption of water by a colloid particle is several molecules deep. From our knowledge of Langmuir's theory<sup>13</sup> of adsorption it seems improbable. Again, it is seen from our results that in general even a pressure so low as 40 cm. water column causes the viscosity value  $s$  to decrease appreciably. This has to be explained as due to decreased hydration by this pressure, *i. e.*, even a small shear will tear off some water molecules wrapping the colloid particle. In other words, the hydration will have to be assumed to be very labile and decreasing with increasing shearing force and hence causing the decrease in the viscosity values.

In diluted sols it is expected that a colloid particle is hydrated to a greater extent than in concentrated ones and as a consequence one expects the increase in the value of  $s$  with progress of dialysis and the fall in the value of  $s$  with increasing shearing force to be more pronounced and rapid with diluted sols than with concentrated ones. Our experimental results, on the other hand, show that in the case of diluted sols the increase in the value of  $s$  with the progress of dialysis and the decrease in the value of  $s$  with increasing shearing force is not so marked as in the case of the concentrated sols.

In our opinion the sols which are specially viscous and yield gels have a distinct orientation of particles even when present in the liquid condition. Certainly, this orientation increases as the electric charge on the colloid particles is decreased. Continued dialysis gradually lowers the electric charge on the colloid particles, which we have measured by the coagulation experiments and hence we find that the value of  $s$  remarkably increases as the sol is purified by the process of continued dialysis. At high pressures, this orientation of colloid particles is



destroyed to a greater degree than at low pressures and hence the percentage increase of  $s$  is less with high pressures than with lower ones as the sol is dialysed. In the case of the diluted sols, this orientation is not so marked because of smaller concentrations of the colloid aggregates and, therefore, the effect of varying shearing force is not so pronounced in this case as with concentrated sols.

It has been suggested by us about two years ago<sup>2</sup> that the force which causes this arrangement or orientation of particles originates from a 'loose crystallographic force'. In our experiments with soaps, gelatine and agar we have shown that all these highly viscous lyophilic colloids possess an orientation of the colloid particles and either stirring these sols or sowing them with an already formed gel of the same concentration facilitates this orientation to a great extent and we get increased viscosity. This is similar to a release of supersaturation from a supersaturated solution of dissolved substances by the crystallographic forces. Our results of sowing the sol of ferric phosphate with an already formed gel are given below:—

Table 5.

Effect of sowing with formed gel. Temperature =  $22^\circ\text{C}$ .

| Pressure<br>Cms. water column | $S(\text{sol})/\eta_\omega$<br>ordinarily | $S(\text{sol})/\eta_\omega$<br>after sowing with already<br>formed gel of $\text{FePO}_4$ |
|-------------------------------|---|---|
| 40                            | 10.481                                    | 10.962  |
| 50                            | 10.121                                    | 10.601  |
| 60                            | 9.942                                     | 10.392  |
| 70                            | 9.667                                     | 10.108  |

It may be mentioned here that the concentration, electrical conductivity and the stability of ferric phosphate sol were not changed by sowing.

The rigidity in the case of lyophilic colloids has been found to exist in measurable amounts by several investigations.<sup>1\*</sup> We are of opinion that this distinct rigidity observed with highly viscous sols is due to a certain orientation of the colloid particles originating from the forces which are inherent on the solid surface to form bigger aggregates. High hydration of colloid particles, however, checks the actual aggregation. The force, which causes this orientation of colloid particles of the sol is also of the smaller magnitude and hence the rigidity is not high and the sol for a particular shearing force behaves as a liquid.

We are, therefore, of opinion that the lyophilic colloids like gelatine, agar, silicic acid, ferric phosphate, etc., show a high viscosity due to an orientation of the colloid particles rather than due to the high hydration of the dispersed phase.

Each of these sols should show a curvilinear viscosity/concentration relation and should also show a remarkable difference in the so-called viscosity with different rates of shear, *i.e.*, will show the property of plastic flow.

It is needless to mention that the simple conception of the viscous flow as advanced by Maxwell for gases does not remain simple in the case of liquids and in its turn becomes more complex in the case of the sols. It appears to us that the so-called viscosity  $s$  cannot be regarded as the true viscosity of the sol and may be termed as the coefficient of structural flow for a definite rate of shear.

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# INFLUENCE OF TEMPERATURE AND LIGHT INTENSITY ON PHOTOSYNTHESIS AND RESPIRATION AND AN EXPLANATION OF "SOLARISATION" AND "COMPENSATION POINT."

By N. R. DHAR,

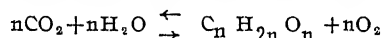
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Received January 11, 1933.

## ABSTRACT

1. The Arrhenius relation connecting velocity and temperature of a reaction which is applicable to ordinary chemical reactions, is not valid in the case of the influence of temperature on photosynthesis and respiration in plants. The non-applicability of the Arrhenius relation to photosynthesis and many other phenomena in plant life can be explained from the following considerations—

(a) It appears that in plant life, the following opposing reactions are taking place :



The direct action (photosynthesis) is being opposed by the reverse reaction (respiration) which increases according to the law of mass action with increase in the concentration of carbohydrates formed from photosynthesis.

(b) There is reason to believe that the velocity of respiration in plants is appreciably accelerated by light.

(c) The influence of temperature on respiration appears to be greater than that on photosynthesis.

2. The greater influence of temperature on photosynthesis in presence of strong light than that in weak light can be explained from the foregoing considerations. Hence, it is needless to assume that there are two reactions involved in photo-synthesis.

3. The observations of Willstätter and Stoll that leaves of low chlorophyll content show a lower acceleration of photosynthesis with increase in temperature than the leaves of high chlorophyll content have also been explained from the same point of view.

4. The experiments of Willstätter and Stoll showing that in chlorophyll rich leaves an increase of light intensity does not affect photosynthesis have been explained from the view point of "exhaustion effect" as observed in ordinary photochemical reactions.

5. That oxygen is essential for photosynthesis appears to be due to the fact that plant life depends on oxygen respiration and the activity of the plant and along with it its photosynthetic power depend on its respiratory activity.

6. The photosynthetic activity is exceedingly high in young leaves and is not proportional to the chlorophyll content. This is because that the respiratory activity of young leaves is very high. In plant life, as well as in animal life, metabolism decreases with age.

7. In plant life in the absence of iron compounds, respiration and photosynthesis become defective as in chlorotic plants, because iron compounds accelerate respiration.

8. It appears that the factor which really controls plant life is its respiratory or metabolic activity.

9. In the animal world, the length of life depends inversely as the rate of living. The duration of the catalytic activity of an active catalyst appears to be short. These considerations

are applicable to plant life as well. In leaves, poor in chlorophyll, the time factor appears more slowly than in chlorophyll rich leaves. In other words, the activity of chlorophyll rich leaves would last for a shorter period than that of chlorophyll poor leaves.

10. The phenomenon of "solarisation", that is, the disappearance of carbohydrates formed from photosynthesis after prolonged illumination appears to be due to respiration, that is, their oxidation by oxygen in presence of light. The respiration, that is, the oxidation of carbohydrates is also increased by increase of temperature caused by light absorption.

11. The compensation point, that is, the light intensity at which the photosynthetic and respiratory activities of plants compensate each other, decreases with decrease of temperature. A certain light intensity which at 20° represents the compensation point, causes an evolution of oxygen due to photosynthesis at 5°. In nature, under certain conditions and at high temperature, the plant cannot store any material due to photosynthesis on account of high respiratory activity, whilst at low temperatures, with the same light intensity, food materials are formed by photosynthesis. The above results have been explained from the following considerations:

(i) Photosynthesis is proportional to the light intensity, there being no photosynthesis in dark.

(ii) Respiration takes place in the dark but is appreciably accelerated by light.

(iii) An increase in temperature affects more markedly respiration than photosynthesis.

12. Respiration appears to be the more fundamental reaction in plant and is more important to plant life than photosynthesis which predominates in plants only under restricted conditions of temperature and light intensity.

#### INFLUENCE OF TEMPERATURE ON RESPIRATION

The influence of temperature on respiration has been investigated with plants and animals. Generally an increase of temperature leads to an increase in the respiration of plants and animals.

Miss Matthaei (1904) determined the carbon dioxide evolution of 2 grams of cherry laurel leaf per hour at various temperatures. From the experiments of Miss Matthaei a smooth curve has been plotted and the following results are obtained from the curve: -

| Temperature.   | CO <sub>2</sub> evolution in gm. | Temperature coefficient for a 10° rise of temperature observed. | Temperature coefficient for a 10° rise calculated from Arrhenius equation. |
|----------------|----------------------------------|---|--|
| 5° }<br>15° }  | 0.000085<br>0.00032              | 3.76  | 3.76   |
| 10° }<br>20° } | 0.000175<br>0.000485             | 2.77  | 3.55   |
| 15° }<br>25° } | 0.00032<br>0.000585              | 1.83  | 3.44   |
| 20° }<br>30° } | 0.000485<br>0.00094              | 1.94  | 3.30   |

When the temperature is higher than 30°, marked variation in the amount of respiration is observed and Miss Matthaei obtained the following results with 2 grams of cherry laurel leaf

| Temperature. | CO <sub>2</sub> evolution in gm. |
|--------------|----------------------------------|
| 38°·3        | 0·00205                          |
| 38°·3        | 0·00230                          |
| 40°·9        | 0·0014                           |
| 40°·9        | 0·0016                           |
| 42°·9        | 0·0015                           |
| 42°·9        | 0·0014                           |

More or less similar variations are observed with photosynthesis at higher temperatures.

The experiments of Kuijper (1910) on the respiration of active seedlings of the lupin, pea and wheat at various temperatures are in general agreement with those of Miss Matthaei. The following results have been obtained from a smooth curve plotted with the values on respiration recorded by Kuijper with pea at different temperatures:—

| Temperature.   | CO <sub>2</sub> evolved in milligrams. | Temperature coefficient for a 10° degree rise of temperature. | Temperature coefficient for a 10° rise calculated from Arrhenius equation. |
|----------------|--|---|--|
| 0° }<br>10° }  | 3·5<br>11·5                            | 3·27  | 3·27   |
| 5° }<br>15° }  | 6·5<br>17·5                            | 2·7   | 3·14   |
| 10° }<br>20° } | 11·5<br>27·5                           | 2·4   | 3·02   |
| 15° }<br>25° } | 17·5<br>46·5                           | 2·6   | 2·91   |
| 20° }<br>30° } | 27·5<br>58·0                           | 2·1   | 2·80   |

The experiments of Kuijper show that there is fluctuation in the amount of carbon dioxide evolution at temperatures higher than 30°. At temperatures higher than 35°, there is a steady reduction in the amount of carbon dioxide given out with time. Hée (Thèse, Paris 1930) also obtained high values of temperature coefficients of respiration with some plants.

Müller-Thurgau and Schneider-Orelli (1910) obtained some peculiar results on the influence of temperature on the respiration of potato tubers. They reported that when the tubers are heated to 40° for some hours, the respiration activity

increases even when the tubers are brought to room temperature and a permanent increase in respiratory activity is observed when the tuber is heated to 44°. These results are different from those obtained by Miss Matthaei and Kuijper who believed that there are two different processes involved in plant respiration, one of which is accelerated and the other retarded by increase of temperature. Müller-Thurgau and Kuijper realised that the influence of temperature on respiration will vary with the nature of the available material undergoing oxidation in the plant. It will be of interest to note that de Boer (1928) reported that in *Phycomyces*, the normal oxidation of fats takes place at low temperatures, whilst at high temperatures carbohydrates are more easily assimilated.

Lundegardh (1924) advanced the view that the temperature-respiration curves can be divided into four sections. In the first section, which goes up to 40°, the curve shows a steady increase of respiration with increase of temperature and in this region the temperature coefficient of respiration for a 10° rise of temperature varies from 1.9 to 3.3. From 40° to 46°, a rapid rise of respiration is observed. In the third section from 46° to 50°, a rise is obtained with an optimum at 50°, above which there is a rapid fall of respiration.

Several plant physiologists believe that the respiration of higher plants increases with increase of temperature according to the van't Hoff rule. Thus Kuijper, Harder (1915) working at temperatures 5° and 25° and Plaetzer (1917) with *Cladophora* obtained the value 2 for the temperature coefficient of respiration for a 10° rise of temperature and Noak (1920) reported the value 1.8 in the respiration of thermophilous fungi. It is well-known that the Arrhenius relation  $\log_e \frac{k_1}{k_2} = \frac{A(T_1 - T_2)}{T_1 T_2}$

is applicable to chemical reactions (where  $K_1$  and  $K_2$  are the velocities of the reaction at  $T_1$  and  $T_2$  absolute temperatures and  $A$  is a constant) and the application of this relation to physiological processes is certainly more correct than to apply the van't Hoff rule, that the temperature coefficient of a chemical reaction varies from 2 to 3 because there are several chemical changes of which the temperature coefficients are much greater than 3 and in many cases, the temperature coefficient may be as high as 7 for a 10° rise of temperature. From the tables recorded above, it will be observed that the Arrhenius relation which is applicable to chemical reactions, does not apply to the problem of plant respiration. The values calculated according to the Arrhenius equation are always greater than those observed.

Recently Crozier (1924-25) has attempted to apply the equation of Arrhenius as modified by Marcelin and Rice to the results on respiration at different temperatures. The Arrhenius constant  $A$  has been designated by Crozier as "temperature characteristic" and he believes that there are three values of "temperature characteristic" for respiration.

It has been reported that with succulents at low temperatures, incomplete oxidation of sugar takes place and organic acids are generated and the respiratory quotient  $\text{CO}_2/\text{O}_2$  is less than unity. When the temperature is increased, sugar is com-

pletely burnt to carbon dioxide and water and the respiratory quotient becomes unity.

It is well known that photosynthesis can go on at low temperatures, respiration also continues with seeds lichens and mosses at low temperatures even up to  $-25^{\circ}$ .

From the foregoing results on the influence of temperature on plant respiration, a very important conclusion can be drawn which is this:—That the influence of temperature on respiration is greater than that on photosynthesis. The results of Miss Matthaei on photosynthesis show that the temperature coefficients of photosynthesis between  $0^{\circ}$  and  $10^{\circ}$  and  $10^{\circ}$  and  $20^{\circ}$  are 2.71 and 2.21 respectively, whilst her results on respiration are 3.76 between  $5^{\circ}$  and  $15^{\circ}$  and 2.77 between  $10^{\circ}$  and  $20^{\circ}$ . The respiration temperature coefficients of Kuijper give the value 3.27 between  $0^{\circ}$  and  $10^{\circ}$ . Similar results have been obtained by Hée and other workers. This important relation that in general, temperature affects respiration more markedly than photosynthesis in plants plays an important rôle in the economy of nature. This difference in temperature effect considerably affects the equilibrium in the amount of photosynthesis and respiration in plants. In a subsequent section the importance of this relation in explaining many plant processes will be discussed.

In cold-blooded animals, which are somewhat allied to plants the respiratory exchange always increases with increasing temperature. With several varieties of flies *Oyclodes gigas*, fishes, etc., marked influence of temperature on respiration has been reported.

#### INFLUENCE OF LIGHT ON RESPIRATION

Although several authors notably Moleschott, Selmi and Pott observed that the expiratory exchange of animals (e.g., dog, mouse, frogs, etc.) is higher in light than in darkness, the experiments of Loeb on chrysalides of butterflies and Ewald on curarized frogs do not warrant the same conclusion.

The investigation on the influence of light on the respiration of green plants becomes complicated because on illumination, the carbon dioxide and water produced in respiration undergo photosynthesis to reform the carbohydrates and other food materials. Borodin (1876) showed that leafy shoots undergo respiration more vigorously after an exposure to light. Miss Matthaei observed that the respiration of a leaf in the dark falls off continuously, whilst on illumination lasting for four or five hours the respiratory values may be doubled and that the increase in respiration is not concomitant with the amount of carbon dioxide assimilated. Moreover Rose (1910) reported a high intensity of respiration in green plants in bright sunshine. Recently Shri Ranjan (1932) has observed increased respiration on illumination with croton, free from chlorophyll. Spoehr (1915) has reported that during the day, the respiration of plants is increased. Moreover, Middleton (1927) with barley seedlings and Whimster with *Pelargonium zonale*, have reported

a marked increase of respiration in air ionised by the radioactive element polonium.

From the foregoing observations the author has come to the conclusion that although in presence of light, the materials available for respiration increase due to photosynthesis and this leads to an increase in respiration, the chemical changes involved in the oxidation of food materials are also accelerated by the absorption of light. Moreover Dhar and collaborators have shown that the food materials like starch, sugars, proteins and fats in aqueous solutions or suspensions are oxidized to carbon dioxide and water by simply passing air at the ordinary temperature in presence of sunlight. In absence of light, there is no oxidation. In presence of inductors like ferrous hydroxide, cerous hydroxide, glutathione, the food materials are oxidized to carbon dioxide and water by air even in absence of light. In presence of sunlight these induced oxidations are greatly increased. It appears, therefore, that the light absorbed by the plants will also accelerate the oxidation of glucose and other food materials present in the plant. Hence in presence of light the respiration in the plant is likely to be increased.

The author is definitely of opinion that light increases plant respiration as much as animal respiration but the influence of light on respiration is less marked than on photosynthesis.

It is well-known that the Arrhenius equation  $\log_e k_1/k_2 = A (T_1 - T_2)/T_1 T_2$  is applicable to ordinary chemical reactions taking place in a homogeneous system ( $k_1$  and  $k_2$  are the coefficients of the velocities of the reaction at  $T_1$  and  $T_2$  absolute temperatures and  $A$  is a constant).

In a publication, Dhar (1920) has shown that the application of the above Arrhenius relation connecting the velocity and temperature of a reaction is certainly more correct than to apply the van't Hoff rule that the temperature coefficient of a chemical reaction for a ten-degree rise of temperature lies between 2 and 3, because the temperature coefficient does not remain constant at different temperature intervals but falls off with increase of temperature. Moreover Dhar (1917) has shown that for some reactions, the temperature coefficient can have the high value 7.2 for a 10° rise.

Many plant physiologists following the lead of Blackman have applied the van't Hoff rule to plant temperature studies. Thus Stiles (Photosynthesis 1925) states. "Many plant and animal processes have been shown to obey the van't Hoff rule, if only approximately and within limits," and "similar curves for the respiration of higher plants have been constructed by Kuijper, who found the van't Hoff rule followed between 0° and 20°." The application of the Arrhenius relation has been found to be general with ordinary chemical reactions. When the same relation is applied to the results actually obtained regarding the influence of temperature on photosynthesis in plants, it fails, as will be evident from the following table obtained from Warburg's results;—



| Light intensity | Observed               | Calc.  |
|-----------------|------------------------|--|
|                 | $\frac{k_t + 10}{k_t}$ | $\frac{k_t + 10}{k_t}$                                     |
| 16              | 2.0                    | 4.11 between 16° and 25° (taking 4.7 between 5° and 10°)   |
| 45              | 2.1                    | 4.01 between 10° and 20° (taking 4.3 between 5° and 10°)   |
| 45              | 1.6                    | 3.66 between 20° and 30° (taking 4.3 between 5.4° and 10°) |

The results have been calculated by applying the Arrhenius relation. It appears that the temperature coefficients of photosynthesis do not obey the Arrhenius relation, which has been found to be universally applicable to ordinary chemical reactions investigated so far and no case of failure has been reported. In photosynthesis the observed values are always smaller than the calculated values. The reasons of the non-applicability of this relation to photosynthesis in plants are:—(1) the greater influence of temperature on the respiration process than that on photosynthesis and (2) the harmful influence of high temperatures on the chloroplast.

It has already been stated that when the temperature of a plant system undergoing photosynthesis is increased the velocity of photosynthesis is increased but to a smaller extent than that of respiration. Consequently, the temperature coefficient of the observed photosynthesis will appear to be smaller than when the reversible reaction was not present. Moreover, the chloroplast in the protoplasmic cell which is likely to be active in the photosynthetic process starts undergoing deterioration when the temperature is greater than 20° and may be partially destroyed when the temperature is still greater. This is evident on comparing the results obtained by Warburg and those calculated from the Arrhenius relation. The observed temperature coefficients between 16° and 25° and between 10° and 20° are nearly half of the calculated values, whilst the observed temperature coefficient between 20° and 30° is much less than half of the calculated value. The pernicious influence of high temperature on physiological and enzyme and bacterial processes is well known. In most cases the optimum temperature in these reactions is round about 20°. Moreover in plant photosynthesis, there is an additional factor namely, the reverse reaction, *e.g.*, respiration which is also simultaneously going on and is counterbalancing the photosynthetic reaction and hence, the influence of temperature on photosynthesis is less pronounced due to these counteracting agencies.

It has already been stated that in the case of some chemical reactions, the temperature coefficient can have the high value 7.2. Hence it is no wonder that the temperature coefficient of photosynthesis at low temperatures (say between 5° and 10°) has the value 4.3. It seems probable that the photosynthetic reaction is not an adsorption process of which the average temperature coefficient is in the

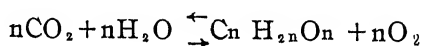
neighbourhood of 1.2 for a ten-degree rise of temperature, but it is controlled by a truly photochemical change having a moderately high temperature coefficient. In several communications from these laboratories it has been shown that photochemical reactions need not have temperature coefficients approaching unity but can have values as high as 4. From the foregoing considerations, it is clear that it is needless to assume that the photosynthetic process involves two reactions. It is believed that in high light intensity the chemical reaction ("Blackman reaction" as designated by Warburg) is determining the total velocity of the reaction, because for a ten-degree rise of temperature between 15° and 25°, the velocity of the photosynthesis is doubled. On the other hand, in low light intensity, the temperature coefficient instead of being 2 as with intense light, is 1.06 and hence it has been assumed that the chemical reaction is not the controlling factor as in the previous case; but the photochemical reaction with a low temperature coefficient determines the photosynthetic rate at low intensities of light.

In presence of intense light, the photochemical reaction causing the photosynthesis and having a moderately large temperature coefficient is predominant and the counteracting influence of the respiration process, which is not as much accelerated by light as the photosynthetic reaction, is not prominent. On the other hand, in presence of feeble illumination, the velocity of the photosynthetic reaction is not high, because this reaction takes place only in light and is proportional to the light intensity. In this case, the counter-acting influence of respiration, especially at increased temperatures, becomes prominent and hence the influence of temperature on the observed photosynthetic rate is feeble.

Warburg (1919) has observed that the temperature coefficient of photosynthesis with the unicellular alga *Chlorella* is much less when the light intensity is feeble than it is strong. Thus  $\frac{k_t + 10}{k_t}$  between 16° and 25° with light intensity 16=20 and  $\frac{k_t + 10}{k_t}$  between 15° and 25° with a relative intensity of 1=1.06.

These results which appear to have been confirmed by other workers can be explained in the following way:—

It has already been stated that in a plant, the following opposing reactions are taking place:



and the temperature coefficient of photosynthesis is less than that of respiration. Hence, when the light intensity is feeble, the velocity of photosynthesis is small and is slightly greater than that of respiration at the same temperature. Now when the temperature of the system is raised through ten degrees, the velocity of the photosynthesis will be increased to a smaller extent than that of respiration. Consequently the temperature coefficient of the observed photosynthesis may be unity or less.

It will be interesting to note in this connection that Harder (1915) working with low light intensity and sea plants of the polar region obtained the following ratio of  $\frac{\text{photosynthesis}}{\text{respiration}}$  for different temperatures:—

|         |        |        |        |
|---------|--------|--------|--------|
| 20°—22° | 0.5882 | 0.4227 | 0.4280 |
| 2°—3.5° | 1.603  | 0.9207 | 2.059  |

Moreover, in nature when the temperature of the air is high, the plants gain no material through photosynthesis because of the high respiration, whilst at lower temperatures with the same light intensity, food materials are formed in the plant.

Willstätter and Stoll (1918) have reported that leaves of low chlorophyll content exhibit a lower acceleration with increasing temperature than the leaves of high chlorophyll content. Thus leaves of *Ulmus* with low chlorophyll content showed a temperature coefficient of 1.34 and with high chlorophyll content of 1.53 between 15° and 25°. These results of Willstätter and Stoll can be explained from the view point already advanced.

The important researches of Willstätter and Stoll show that although there are minor discrepancies, the rate of photosynthesis is determined by the chlorophyll content of the plant. Hence in presence of large amounts of chlorophyll in the leaves, the velocity of the photochemical reaction involved in the photosynthetic process will be larger than in the case of leaves containing smaller quantities of chlorophyll. In the case of leaves containing large amounts of chlorophyll, the direct photochemical process being high the reverse reaction of respiration will appear to be less pronounced and this case is comparable to the case previously discussed with high light intensity and hence, temperature increase will lead to an increase of photosynthesis. On the other hand, in presence of small amounts of chlorophyll in the leaves, the photosynthetic rate is low and hence the opposing respiration reaction will appear to be prominent and this case is allied to photosynthesis with low light intensity having a small temperature coefficient.

Willstätter and Stoll obtained the following interesting results:—

Photosynthesis of the green and yellow varieties of Elm 5%CO<sub>2</sub> and 24000 Lux.

| Variety          | Temp. | Dry weight<br>of leaves | Leaf sur-<br>face<br>sq. cm. | Chlorophyll<br>mg. | Photosynthesis<br>grm. CO <sub>2</sub> hour |                     |     |
|------------------|-------|-------------------------|------------------------------|--------------------|---|---------------------|-----|
|                  |       |                         |                              |                    | 8 grms<br>fresh<br>leaves                   | 1 sq. m.<br>surface |     |
| Chlorophyll poor | 25°   | ...                     | 2.00                         | 321                | 0.95  | 0.075               | 2.3 |
| „                | „ 15° | ...                     | 2.00                         | 321                | 0.95  | 0.056               | 1.7 |
| Chlorophyll rich | 25°   | ...                     | 2.35                         | 421                | 13.0  | 0.089               | 2.1 |
| „                | „ 15° | ...                     | 2.35                         | 421                | 13.0  | 0.058               | 1.4 |

The foregoing results show that the temperature coefficient (1.53) of the photosynthesis with chlorophyll rich leaves is greater than that with chlorophyll poor leaves (1.34), although the photosynthesis is not at all proportional to the amount of chlorophyll in the leaves. Willstätter and Stoll find that temperature variations do not affect the rate of photosynthesis of the yellow varieties as much as the normal ones. In the yellow varieties, the amount of photosynthesis being small, the compensating influence of respiration becomes prominent and hence temperature does not appear to influence photosynthesis with these varieties to the same extent as the normal ones with more chlorophyll.

Moreover, differences in light intensity have more profound effect on the yellow varieties than on the normal ones and the time factor appears more slowly than with the normal ones. It is well-known that photosynthesis increases with the light intensity and the chlorophyll content of the leaves. Now in the case of leaves containing much chlorophyll, the velocity of photosynthesis will be high and may reach the maximum, even when the light intensity is not high and hence in these cases, the reaction will be less sensitive to the influence of light changes, because the reaction is already fast due to the presence of large amounts of chlorophyll. On the other hand, when the chlorophyll content is small, the reaction velocity is small and light will affect the velocity more markedly than in the previous case. This explanation is in agreement with the observations of Willstätter and Stoll that in the chlorophyll rich leaves, an increase of light intensity was without influence on photosynthesis; in fact the light intensity could be reduced by  $\frac{3}{8}$  without affecting the rate of photosynthesis. Exactly similar exhaustion effect has been observed with several photochemical reactions where the velocity of the reaction may be proportional to  $I^{\frac{1}{2}}$  or  $I^{\frac{1}{3}}$  in some cases where the reaction is very fast.

#### RESPIRATION—THE MOST FUNDAMENTAL OF THE PLANT PROCESSES

It seems that in plants as much as in animals, respiration is the most fundamental process, that is going on in the plant system. Photosynthetic activity is a subsidiary reaction, in comparison with respiration. It appears that the various processes which are associated with plant life can only take place as long as respiration lasts.

The activity of a plant is measured by its respiration. It appears that the greater the rate of respiration per unit surface, the greater is the activity of the plant. The amount of respiration would depend on (1) the concentration of carbohydrates and other food materials available in the plant and (2) a minimum oxygen pressure and (3) the activity of the enzymes and inductors. When factors (2) and (3) are constant, respiration will depend on the concentration of carbohydrates, proteins and other food materials, which is controlled by the photosynthetic activity of the plant.

The view that respiration is more fundamental in plant life than photosynthesis is supported from the following observations:—

Warburg has reported that, while respiration is not influenced by different partial pressures of oxygen above a certain minimum, photosynthesis is less at

higher pressures. A change in the partial pressure of oxygen from  $\frac{1}{50}$  to 1 atmosphere reduces the photosynthetic rate by about  $\frac{1}{3}$ .

Wurmser and Jacquot (1923) have observed that when certain marine algae are subjected to temperature from 36° to 45° for 1 to 15 minutes, the rate of photosynthesis is always depressed when the plants are returned to the temperature of the environment (16°). Similar effects are produced with glycerol. Warburg has shown that photosynthetic rate is reduced by hydrocyanic acid and urethanes in extreme dilutions in which the respiratory activity is not affected and in certain cases, even stimulated. It appears, therefore, that photosynthetic process is more sensitive than that of respiration. As all plant processes depend on respiration, which is the vital reaction in plant life as much as in animal life, photosynthetic activity cannot proceed without respiration taking place in the plant and hence, without the presence of oxygen, which supports respiration in both plant and animal life. Because lack of oxygen is detrimental to respiration, it is also harmful to photosynthesis. Consequently, the classical experiments of Boussingault (1868) and Pringsheim (1887) showing that in an atmosphere of hydrogen, nitrogen, carbon dioxide, or methane plants lose the power of photosynthesis, are easily explained from the above view point, because in presence of these gases, oxygen respiration stops. It appears, therefore, that besides light, chlorophyll, carbon dioxide and moisture supply, respiration is also necessary for photosynthesis.

Willstätter and Stoll have observed that various plants exhibit a wide variation in their resistance to lack of oxygen. According to Willstätter and Stoll, the partial pressure of oxygen can be reduced to  $1/100^{\text{th}}$  of that in air without affecting photosynthesis if the rest of the atmosphere is nitrogen. After complete displacement of oxygen for two hours, the leaves on illumination cannot effect photosynthesis, although under these conditions, the leaves show no visible signs of injury. When *Cyclamen europaeum*, *polytrichum juniperinum* are exposed to oxygen free atmosphere for one hour, the photosynthetic activity is decreased but not entirely stopped. When the plants are kept in oxygen free atmosphere for 15 to 24 hours, they show no photosynthesis immediately on illumination, but after half an hour or so, photosynthesis begins and continues to a high rate. Long continued exposure to oxygen free atmosphere produces injurious effect on the photosynthetic mechanism. The longer the time of exposure of a plant to an atmosphere, free from oxygen, the lower is the rate of subsequent photosynthesis and more incomplete the recovery. Willstätter and Stoll have concluded from their careful experiments that oxygen is essential for photosynthesis but a small quantity of oxygen is enough for photosynthesis. Now, as soon as photosynthesis begins, oxygen is generated and respiration goes on. Lack of oxygen produces a permanent injury to the plant, because respiration which is the most important of the plant processes stops in the absence of oxygen. Moreover, it appears from the foregoing results, that for plants, the oxygen requirement for respiration

is less than in animals and they resist lack of oxygen in their living atmosphere much better than animals.

It has already been stated that the activity of a plant is measured by the amount of its respiration per unit surface. Consequently, the greater the respiration, the greater the activity of the plant and greater the photosynthesis, because photosynthesis, like other plant processes, is associated with the activity of the plant. It has already been stated that in plants, Willstätter and Stoll did not find any direct proportionality between the chlorophyll content and its photosynthetic activity. This is explained from the view-point advanced here that the respiratory activity of the plant is the most vital of the plant processes and all other functions of the plant depend on the respiratory activity and consequently, photosynthetic rate is likely to be more directly proportional to the respiratory activity than to any other single factor, *e.g.*, chlorophyll content, light intensity or carbon dioxide concentration. Experiments are in agreement with this view-point. Plester (1912) showed that the leaves of the light green or yellow varieties have a lower rate of photosynthesis and respiration than the varieties rich in chlorophyll. Although, there is no parallelism between chlorophyll content and photosynthetic rate, the ratio  $\frac{\text{respiration}}{\text{photosynthesis}}$  appears to be constant as will be evident from the following results obtained by Plester with the light green varieties:—

Ptelea=1'77, Catalpa = 1'72, Mirabilis=2'0, Ulmus=2, Populus=2'12. Similar results correlating respiration and photosynthetic rate have been obtained by Miss Henrici (1918) with alpine and low land plants, Boysen-Jensen (1918) and Spoehr and McGee (1923).

Willstätter and Stoll have also studied the photosynthetic activity of leaves of different ages. They have compared the activity of a light green leaf from the end of a branch with that of a dark green leaf from the base of the same branch. Their results are given below:—

*Photosynthesis of leaves from the same plant but in different stages of development at 25°—5% CO<sub>2</sub> and 4800 Lux.*

| Species                 | Date    | Description of leaves.                   | 10 gm. fresh leaves |                           | Photosynthesis<br>gm. CO <sub>2</sub> per hour |                                | Photo-synthetic number<br>P <sub>c</sub> |
|-------------------------|---------|--|---------------------|---------------------------|--|--------------------------------|--|
|                         |         |  | Dry weight<br>grms. | Chlorophyll<br>milligram. | Per 1 gm.<br>dry weight.                       | Per 1 sq.<br>dm. leaf<br>area. |  |
| Acer pseudo<br>platanus | June 23 | 4th to 6th leaf<br>from end of<br>branch | 3.3                 | 8.3                       | 0.030  | 0.016                          | 11.8                                     |
|                         | June 24 | From base of<br>branch                   | 3.58                | 40.0                      | 0.058  | 0.026                          | 5.2                                      |

| Species       | Date    | Description of leaves.             | 10 gm. fresh leaves. |                       | Photosynthesis gm. CO <sub>2</sub> per hour. |                          | Photosynthetic number P <sub>c</sub> |
|---------------|---------|------------------------------------|----------------------|-----------------------|--|--------------------------|--------------------------------------|
|               |         |                                    | Dry weight grms.     | Chlorophyll milligram | Per 1 gm. dry weight                         | Per 1 sq. dm. leaf area. |                                      |
| Tilia cordata | June 25 | Young light green                  | 2.56                 | 6.5                   | 0.036  | 0.018                    | 14.2                                 |
|               | June 26 | Lower dark green from same branch  | 3.19                 | 28.1                  | 0.058  | 0.028                    | 6.6                                  |
| Laurus        | June 30 | Light green leaves                 | 3.10                 | 12.7                  | 0.024  | 0.019                    | 5.9                                  |
| Nobilis       | July 1  | Dark green leaves of previous year | 4.95                 | 21.2                  | 0.023  | 0.023                    | 3.7                                  |

The foregoing results of Willstätter and Stoll on the photosynthetic activity of leaves in different stages of development show that although the chlorophyll content of the leaves increases and the photosynthetic activity also increases, the two are not parallel. Consequently, it is clear that with the young leaves, the photosynthetic activity is exceedingly high and is not proportional to their chlorophyll content, because the respiratory activity of the young leaves is also very high. In other words, the greater the respiratory activity (metabolism), the greater is the photosynthetic activity.

The photosynthetic activity of etiolated plants in which the chlorophyll is just developing, shows the disproportionality between photosynthesis and chlorophyll content. Willstätter and Stoll, using cultures of *Phaseolus Vulgaris* and *Zea mays*, found that they are remarkably active, as soon as the first traces of chlorophyll are formed in light. Thus *Phaseolus* with a chlorophyll content of 0.7 milligram per 10 grams of fresh leaves, had a photosynthetic number (P<sub>c</sub>)=133, whilst the control plants grown in light with 18.6 milligrams chlorophyll per 10 grams of leaves showed a photosynthetic number of 9.4. In general, the photosynthetic number of etiolated leaves is much higher than that of young leaves which developed in the light. This is certainly due to the fact that the respiratory activity of the etiolated leaves is much greater than that of young leaves which developed in the light.

#### INFLUENCE OF IRON COMPOUNDS ON PLANT RESPIRATION

Moreover, the relation of photosynthesis and chlorophyll content of chlorotic plants is of great interest from this point of view. When plants grow in the absence of materials containing iron salts, they become very pale green or colourless

with limited development of chloroplasts. This happens even under conditions of high illumination intensity. It has already been emphasised that respiration is the most fundamental and vital of the plant processes and factors, which inhibit respiration, also interfere with normal development and growth of plants. It is well known that iron compounds are of great importance to respiration in the animal kingdom. Dhar and his collaborators have shown that food materials are readily oxidised by air or hydrogen peroxide in presence of iron compounds. The iron present in animal blood accelerates the metabolism of food materials in the body. Consequently when the iron content of the blood decreases or the amount of red blood corpuscles becomes less, metabolism of food materials becomes defective, and the person suffers from anæmia or chlorosis. Under these circumstances, iron compounds are used as medicine and these help metabolism.

In plant life also, in the absence of iron compounds, respiration becomes defective and hence the vital activities and growth of the plant are hindered and it becomes chlorotic and poor in chlorophyll content. As the respiratory activity is defective in chlorotic plants, it is expected that its photosynthetic power will also be anomalous. This is borne out from the experiments of Willstätter and Stoll, who cultivated plants with nutrient solutions containing no iron. While other types of leaves also poor in chlorophyll such as the light green or yellow varieties, autumnal and etiolated leaves, showed high photosynthetic activity in comparison with their chlorophyll content, the chlorotic leaves have a low rate of photosynthesis. Hence photosynthesis goes hand in hand with respiratory activity. It is interesting to note here the observations of Curtel (1900) who has reported that chlorotic plants have a lower rate of respiration and transpiration than normal plants.

The important fact brought out by the investigations of Willstätter and Stoll is that the leaves of light-green or yellow variety as far as photosynthesis is concerned, are affected more by differences in light intensity, while the leaves rich in chlorophyll are more sensitive to changes of temperature. These results have already been explained in the foregoing pages from our view-point of the opposing influence of respiration on photosynthesis.

In explaining these and other results Willstätter and Stoll have been led to the assumption of the existence of an internal factor or protoplasmic factor, which is supposed to be of an enzymatic nature. I have put forth the view that this internal factor is really the respiratory activity or metabolic activity of the plant, which is also probably of an enzymatic nature and may depend on the presence of inductors.

#### INFLUENCE OF AGE ON PLANT PROCESSES.

It is a well established fact that metabolism (carbon dioxide output) per unit area decreases with age in the animal world. (Compare Dhar, New conceptions in Bio-chemistry, 1932.) In plant kingdom, the same relation is observed. From



the quantitative work of Willstätter and Stoll on the relations between the rate of photosynthesis, chlorophyll formation and respiration, it is clear that respiratory activity is very high in very young leaves and it decreases with time and development of the leaf. Young leaves have an exceedingly high rate of respiration, which decreases to one-fourth of this rate when the leaf matures. Kidd, West and Briggs (1921) have concluded from a large number of experiments on respiration of *Helianthus annuus* in the laboratory and in the field that the respiratory activity of the entire plant decreases with age. Hover and Gustafson (1926) have observed that the velocity of respiration of the leaves of maize, wheat, oat and sorghum also decreases with age up to middle age. In general, functional activity decreases with age. Under favourable conditions of temperature and light, the development of chlorophyll is rapid. Willstätter and Stoll have observed an increase in photosynthesis with an increase in chlorophyll content. There is, however, no direct proportionality between the chlorophyll content and the photosynthetic rate. This is shown in the following table:

Rate of photosynthesis, chlorophyll content and photosynthetic number at 25°, 5% CO<sub>2</sub>, about 48000 Lux-(results of Willstätter and Stoll).

| From 10 grms. fresh leaves. |                                |                  |                         | Photosynthesis gram CO <sub>2</sub> per hour. |               | Photosynthetic number P <sub>c</sub> |
|-----------------------------|--------------------------------|------------------|-------------------------|---|---------------|--------------------------------------|
| Date.                       | Species.                       | Dry weight grms. | Chlorophyll milligrams. | Per gm. dry weight.                           | Per 1 sq. dm. |                                      |
| April 29 ...                | <i>Aesculus Hippocastanum.</i> | 2.10             | 10.1                    | 0.054   | 0.043         | 11.1                                 |
| May 7 ...                   |                                | 2.06             | 15.1                    | 0.088   | 0.039         | 12.1                                 |
| June 3 ...                  |                                | 2.94             | 24.7                    | 0.054   | 0.033         | 6.4                                  |
| October 8 ...               |                                | 3.62             | 31.2                    | 0.041   | 0.044         | 4.8                                  |
| May 1 ...                   | <i>Sambucus Nigra.</i>         | 1.85             | 11.7                    | 0.078   | 0.046         | 12.2                                 |
| May 8 ...                   |                                | 2.25             | 23.1                    | 0.101   | 0.057         | 9.8                                  |
| July 14 ...                 |                                | 2.56             | 23.5                    | 0.057   | 0.032         | 6.2                                  |

With time, the dry weight of the leaves increases and on the basis of the dry weight, there is a decrease in photosynthesis. The leaves also show a consistent increase in chlorophyll content but this does not involve an increase in photosynthesis. Similar results have been obtained with other leaves.

It is well known that the longevity of cold-blooded animals is much greater than that of warm-blooded animals of the same size. Moreover, amongst warm-blooded animals, the longevity of smaller animals, is in general less than that of large animals. Also the duration of life varies inversely at the rate of energy expenditure during its continuance. In short, the length of life depends inversely as the rate of living. These results can be explained from the view-point that the greater the activity of the cells and the body enzymes the less is the duration of their active life. It has been frequently noted in catalytic operations that the duration of active catalytic influence of a highly active catalyst is short. (Compare Dhar—New Conceptions in Biochemistry, 1932.)

These conclusions appear to be applicable to the plant kingdom. In studying the influence of temperature on photosynthesis, it has been observed that the maximum velocity of photosynthesis cannot be maintained for a long time, but that with time, this maximum rate shifts to a lower temperature. This time factor is of great interest in plant physiology. In leaves poor in chlorophyll, *i.e.*, the light green or yellow varieties, the time factor appears more slowly than in leaves rich in chlorophyll. It has already been stated that chlorophyll rich leaves are more active towards photosynthesis and respiration than the yellow varieties of leaves. Hence the duration of the activity of the chlorophyll-rich leaves at a definite temperature is expected to be less than that of the comparatively inactive variety of leaves containing smaller amounts of chlorophyll. Consequently, the time factor appears more slowly in the less active yellow leaves than in the active chlorophyll-rich leaves. In other words, the activity of the chlorophyll-rich leaf will last for a shorter time than that of the chlorophyll-poor leaf.

#### THE PHENOMENON OF "SOLARISATION"

It is well known that not only high temperature but also long exposure to strong light affects photosynthetic activity. Thus Ursprung (1917) observed that a leaf of *Phaseolus* after five hours of illumination showed very deep coloration of the starch iodine, while after 85 hours of illumination, the reaction was faint. This phenomenon can be observed with almost any source of light of sufficient intensity and the time required is proportional to the light intensity. The effect is first brought about in the red orange portion, the region showing the best photosynthetic activity. With higher intensity, the shorter wavelengths bring about in shorter time and it is apparently proportional to the photosynthetic activity of light. Ursprung has called this phenomenon "solarisation" as it is analogous to the phenomenon of solarisation observed in photographic plates under similar circumstances.

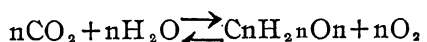
It is expected that not only with starch but with other carbohydrates, similar effect will be observed. This behaviour has been ascribed to the inactivation of chloroplasts. After long exposure to intense light, the plant organs are assumed

not to function, although they are not killed and on keeping in the dark for a period, again produce starch normally.

The inhibiting effect of long exposure to light of high intensity on photosynthesis has long been studied by Ewart (1897) and the inhibiting effect has been ascribed to the destruction of chlorophyll. Pantanelli (1903) explains the fatigue effects observed by him in bright light from the view-points of chlorophyll destruction and injury to the chloroplast plasma. The observations of Ewart on *Allium cepa*, which does not form starch, indicate that when leaves of this plant are exposed to bright light for 14 days or for a shorter period while being fed with sugar, the evolution of oxygen finally ceases. This inactivation apparently does not injure the cells or chloroplasts. After a few days in darkness, the capacity for photosynthesis is regained.

The foregoing facts are explained from the following considerations:

In plants the following equilibrium exists:



The direct action (photosynthesis) is being opposed by the reverse reaction (respiration), which will increase, according to the law of mass action with increase in the concentration of the carbohydrate, which is a product of photosynthesis. Consequently with accumulation of carbohydrates or when the plants are fed with sugar, as was done by Ewart, photosynthesis is retarded and may stop altogether when the carbohydrate content becomes very high. When the illumination is high and it lasts for a long time, the carbohydrate content increases and along with it the respiration also increases, and thus the photosynthetic velocity falls off with time even when the illumination is continued. After a time, the respiration will more than counterbalance photosynthesis and the carbohydrates formed by the photosynthesis will be oxidised to carbon dioxide and water and will disappear on prolonged exposure. When the carbohydrates disappear, the photosynthesis will again begin. It has been known for a long time that the photosynthetic rate decreases with accumulation of the products of photosynthesis. Moreover, Saposchnikoff (1893) has demonstrated the inhibitory power of an accumulation of carbohydrates and that these cannot increase beyond a certain point. When the leaves of *Vitis vinifera* contain 23 to 29 per cent carbohydrates of the dry weight, photosynthesis ceases and respiration predominates. Saposchnikoff has shown that as carbohydrates accumulate, decrease of photosynthetic rate takes place, whilst a decrease in the carbohydrate content results in an increased photosynthesis. These results are evident from the viewpoint of the reversible reactions already put forward.

Moreover, there are two other factors, which increase respiration, should be considered: (1) influence of light intensity on the respiratory process, (2) influence of increased temperature caused by prolonged light absorption. In several publications, Dhar and collaborators have shown that food materials like starch,

sugars, proteins, fats, etc., in aqueous solutions or suspensions are oxidised to carbon dioxide and water by simply passing air at the ordinary temperature in presence of sunlight. In absence of light, there is no oxidation. In presence of inductors like ferrous hydroxide, cerous hydroxide, glutathione, insulin, etc., the food materials are oxidised to carbon dioxide and water by air even in absence of light. In presence of sunlight, these induced oxidations are greatly increased. Hence Dhar and collaborators have suggested that on light exposure the metabolism in the animal body is increased, because the food materials are oxidised to a great extent by air due to the absorption of light. It seems pretty certain that in plants also the respiration or the oxidation of carbohydrates and other food materials, which slowly proceeds in the dark due to the presence of enzymes and inductors, is accelerated on exposure to light. It is well known that several plants and flowers run a temperature higher than that of the surrounding air in the dark due to respiration and these may be roughly compared to warm-blooded animals. In the dark, most plants resemble cold-blooded animals as the plants do not possess thermoregulatory contrivance as in warm-blooded animals, and the plants undergo oxidation and the carbohydrates and other food materials are burnt away. The temperature attained by plants is cumulative. The rise of temperature can be observed by pushing the arm in a heap of lawn cuttings containing a fair amount of clover. Moreover Molisch (1908) observed that the bulked leaves of *Carpinus betulus* attained a temperature of 51° in 15 hours. Pierce (1912) reported a heat gain due to respiration of 8.55 calories per minute per kilogram of germinating peas. The amount of heat generated by germinating peas decreases with age. It is of interest to note that the amount of heat energy generated by the germinating peas is roughly one quarter less than the quantity of heat evolved by a mouse under identical conditions.

In obtaining the energy necessary for its existence, the plant can show a much larger change of weight than the animal. Thus Ramann and Bauer (1911) have recorded that young saplings of deciduous trees show a decrease of 20 to 45 per cent of their dry weight during the period of activity following the winter sleep. It will be of interest to note that the respiratory exchange of hibernating mammals during the awakening is enormously greater than that during the period of sleep. In presence of strong light, the respiration velocity seems to be increased. Moreover when the plant is exposed to strong light for a long time, the temperature of the plant is likely to increase and with increased temperature, the respiration velocity is markedly increased, because the influence of temperature seems to be more pronounced on respiration than on photosynthesis. Consequently, when a plant is exposed to bright light for a long time, respiration more than counterbalances photosynthesis due to the increased concentration of carbohydrates, increased velocity of respiration by the absorption of radiant energy in the form of light and increase in the temperature of the plant by the absorption of light and the conversion of the light rays to heat. Under these circumstances, plants may behave as animals, as far as metabolism is concerned.

## COMPENSATION POINT.

The important facts regarding compensation point are as follows :—

The compensation point, *i.e.*, the light intensity at which the photosynthetic and respiratory activities of the plant compensate each other decreases with decrease of temperature as will be evident from the following table:—

*Spirogyra* 174 at 20°; 26·7 at 5°; *Fontinalis* 150 at 20°; 40 at 5°; *Cladophora* 253·3 at 20°; 62·9 at 5°; *Cinclidotus* 400 at 20; 75 at 5°. The foregoing results show that the light intensity which at 20° represented the compensation point, produced an evolution of oxygen due to photosynthesis at 5°.

With *Cladophora*, with increasing temperature, the compensation point rises more rapidly than the rate of respiration determined in the dark; an increase of temperature from 5° to 25° causes the respiration to become 4·8 times greater in the dark, whilst the light intensity increases to 6·69 times.

The foregoing results as well as other facts on the compensation point can be explained from the following considerations:—

1. Photosynthesis is proportional to the light intensity, there being no photosynthesis in the dark.
2. Respiration takes place in the dark but is appreciably accelerated by light.
3. An increase of temperature affects respiration more markedly than photosynthesis.

The fact that the compensation point rises with increase of temperature is due to the greater increase of respiratory activity than photosynthetic activity with increased temperature. The respiratory activity of the plant, which counterbalances the photosynthetic process, increases much more than photosynthesis at higher temperatures and consequently, the light intensity must be increased to cause more photosynthesis to counteract the increased respiratory activity. There is another reason for further increase in the respiratory activity of the plant. Hitherto, it has been assumed by most of the plant physiologists that the process of respiration is not accelerated by light. But it is evident from the researches of Dhar and collaborators that animal metabolism is markedly accelerated by light absorption. Hence, it seems pretty certain that the respiratory process taking place in plants is also accelerated by light. Consequently, the respiratory activity of the plant is accelerated by two agencies; *e.g.*, temperature and light intensity and thus the light intensity required for increased photosynthesis in order to counteract this high respiratory activity should be very high. Thus with increasing temperature, the compensation point should rise more rapidly than the rate of respiration because of its additional enhancement by light absorption and this is clearly borne out from the experiments on *Cladophora* in which an increase of temperature from 5° to 25° causes the respiration to become 4·8 times greater when determined in the dark, whilst the light intensity increases 6·69 times, for the compensation point.

It is evident that under certain circumstances, when the temperature is high and the light is intense, the compensation point may not be attained even with intense light and the plant will evolve carbon dioxide like an animal even in presence of light. This is likely to happen frequently in tropical countries where at the sea level, the heat rays of the sun become very prominent and the temperature of the plant will be high and photosynthesis cannot counterbalance respiration under these circumstances. At higher altitudes, the light rays are more active than at the sea level and it is expected that at these altitudes, very seldom, respiration will exceed photosynthesis in sunlight. These conclusions are corroborated from the experimental results of Harder (1921) with sea plants in the polar zones where the light intensity is not very high. Thus Harder records the following ratio of  $\frac{\text{photosynthesis}}{\text{respiration}}$  for different temperatures:—

|         |        |        |        |
|---------|--------|--------|--------|
| 20°—22° | 0.5882 | 0.4427 | 0.4280 |
| 2°—3.5° | 1.603  | 0.9207 | 2.059  |

The position of the compensation point of a plant with reference to temperature is naturally of great importance to the life of the plants and its relation to the environment.

Harder has reported that conditions may exist in nature where at higher temperatures, the plant stores no material through photosynthesis on account of the high respiratory activity. While at lower temperatures with the same light intensity, food materials are formed in the plant by photosynthesis.

The experimental observation that the compensation point, (*i.e.*, the light intensity at which the photosynthetic and respiratory activities of the plant compensate each other varies with different plants) is explained on the basis that the respiratory activity of the plant and its increment by temperature and light vary with different plants.

Starting with the same culture of *Cladophora*, and keeping one portion in diffused light and another in direct sunlight, great differences in the compensation point are observed in a week. With *Sinapis alba*, a plant growing in light, the compensation point is at 1.0 (Bunsen units  $\times 100$ ) but a compensation point lying at only 0.2 is observed with *Oxalis acetosella*, a shade plant. Previous illumination of the plant must be considered before any conclusion is drawn from determination of the compensation point, which varies considerably with previous illumination of the plant. It has been observed that under certain circumstances, in Fontanalis, photosynthesis more than counterbalances respiration when the illumination is only 10 lux, whilst under other conditions, 150 lux is insufficient to achieve this.

Under constant and high illumination, leaves of beach tree emits carbon dioxide at 6250 lux; the sun tree, *Robinia*, requires 25 times more intense light for photosynthesis to exceed respiration than the shade tree *Fagus*. According to Lundegardh (1921) the respiration of the shade plant *Oxalis* is lower than that in

the sun plants *Nasturtium* and *Atriplex*. In *Oxalis*, the compensation point occurs in normal air at a light intensity of  $1/120$  to  $1/140$  that of direct sunlight, whilst in the sun plants, the compensation point is attained when the light intensity varies from  $1/40$  to  $1/60$  of direct sunlight.

These experimental observations are explicable from the following consideration:—The temperature of the trees growing in light is higher than that of trees growing in the shade. Hence, the respiratory activity of plants growing in shade is much less than that growing in light. Moreover, the respiration of plants growing in light is also accelerated by the light absorption. Consequently the light intensity required to cause the increased photosynthesis in order to counteract the enhanced respiration due to an increase of temperature and light absorption must be very high.

Moreover, there is another important consideration in the explanation of the higher compensation point of trees grown in light than in the shade. From our experience on the velocity of photochemical reactions taking place in strong light, it is generally observed that the velocity of the photochemical reaction is not directly proportional to the light intensity or the absorbed light but the velocity varies as  $I^n$  where  $n$  is less than unity. On the other hand, in presence of feeble light also the velocity varies as  $I^n$ , in which case  $n$  is unity or more. Consequently, from the quantitative experiments with ordinary photochemical reactions, it is clear that in presence of intense light, photochemical reactions utilise less amount of absorbed radiation than when the same reactions take place in less intense light. This is usually known as "exhaustion effect". It is clear, therefore, that in photosynthesis, the same relation is to be expected. This behaviour has been observed by O. Warburg (1922) in his experiments on the efficiency of the photosynthetic process. It has been reported by Warburg that when plants are cultivated under conditions of high light intensity, they utilise only a small amount of the absorbed energy. Plants grown under conditions of low light intensity can utilise a relatively large proportion of the absorbed energy. Hence the light intensity necessary to obtain the requisite velocity of photosynthesis required to counteract respiration in the case of plants growing in light will be greater than that required for plants cultivated in the shade. Hence by growing the same type of plant under conditions of high and low light intensity, one type apparently passes into the other within a short time and its photosynthetic efficiency and possibly respiratory activity are altered.

From the foregoing pages, it is clear that the contention of Plaetzer (1917) that the value of the light intensity at the compensation point is not a function of the respiratory activity is not correct. Plaetzer in his consideration of the compensation point missed the important point that the respiratory activity is also accentuated by light.

From these considerations, one thing comes out very prominently that respiration is of vital importance to plant and is more fundamental and important

to plant life than photosynthesis, which predominates in the plant only under highly restricted conditions of temperature and light intensity. In other conditions beyond this limit, in light as well as in the dark, plant life enjoys respiratory activity as much as animal life. Hence it appears that respiratory activity controls plant life as animal life.



# CHEMICAL EXAMINATION OF THE FRUITS OF *TRIBULUS TERRESTRIS*, LINN.

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*Tribulus terrestris*, commonly known as small caltrops in English, *chota-gokhru* in Hindi and *gokhuri* in Bengali, is a plant of the natural order Zygophyllæ. It is a well-known medicinal plant of long use in Hindu medicine. 'It has a slender fibrous root 4-5 inches long, cylindrical and of a light brown colour; the odour is faintly aromatic and the taste is sweetish and astringent. From the roots spring 4 to 5 delicate stalks, spreading on the ground; these are hairy and extend to 2½ ft. in length; the leaves are pinnated, leaflets of 5 to 6 pairs, nearly round. The flowers are auxiliary on short peduncles and composed of five broad obtuse yellow petals; these are succeeded by a roundish five-cornered fruit, about the size of a marble, armed with prickles; this ripening divides into five cells, each armed with four strong thorns and containing several seeds. The seeds are oily, and enclosed in very hard stony cells. The plant is common in sandy soil throughout India, and is found plentifully in the United Provinces and in Madras. The matured fruits are sun dried and stored for medicinal uses.

As regards its medicinal properties the Hindus<sup>1</sup> consider the fruit and root as having cooling, diuretic, tonic and aphrodisiac properties; and use them in gonorrhœa and dysuria. It<sup>2</sup> is used in painful micturition, calculous affections, and impotence. *Tribulus terrestris* attracted the attention of European<sup>3</sup> doctors and has been favourably spoken of by them as an aperient and diuretic. An infusion made from the fruit has been found very useful in gout, kidney disease and gravel.

As regards its chemical properties an ethereal or alcoholic extract of the powdered fruits are supposed to yield to water a crystalline residue containing a body precipitated from its solution by ammonia and having the properties of an alkaloid and associated with hydrochloric acid or alkaline chlorides. The fruits also contain a fat and a resin, the latter is probably the source of aroma of the drug, as it gives off a fragrant odour when burnt. The fruits contain a rather large quantity of mineral matter (14.9%).

The above represents the work that has been done on the plant. The present author was tempted to put the fruits under systematic chemical analysis on account of

the crystalline alkaloid supposed to be contained in the plant. Unfortunately, the claims in this direction, put forward by previous workers, could not be substantiated, as will be seen in the experimental part of the paper. The investigation on the fruits has, however, proved the presence of 5 per cent of a pale-yellow semi-drying oil, a peroxidase and a starch hydrolysing enzyme, traces of a glucoside body, large quantity of inorganic matter, a resin, a nitrogenous protein compound and a phlobaphene. The results of examination are recorded in the experimental part of the paper.

#### EXPERIMENTAL.

The dried fruits of *Tribulus terrestris* were obtained from local market. A preliminary experiment was made with the cold hydrochloric acid extract of the powdered drug with alkaloidal reagents, and the following precipitates were obtained:—

|                         |     |     |                               |
|-------------------------|-----|-----|-------------------------------|
| Picric acid             | ... | ... | yellowish-white turbidity.    |
| Sodium carbonate        | ... | ... | White gelatinous precipitate. |
| Phosphomolybdic acid    | ... | ... | White preeipitate.            |
| Mayer's reagent         | ... | ... | do.                           |
| Phosphotungstic acid    | ... | ... | do.                           |
| Dragendorff's reagent   | ... | ... | orange brown precipitate.     |
| Bouchardat's reagent... | ... | ... | brown precipitate.            |
| Platinic chloride       | ... | ... | yellowish white precipitate.  |
| Gold chloride           | ... | ... | precipitate in traces.        |

None of the above precipitate was crystalline. An aqueous extract of a fresh quantity of the drug, however, remained unaffected by the above reagents.

500 c.c. of 2 per cent. hydrochloric acid extract of 200 g. of the powdered material was made alkaline with ammonia. The precipitate was filtered and identified to be inorganic. The filtrate was separately extracted with petroleum ether, chloroform and amyl alcohol, but nothing was extracted by the solvents. The aqueous solution was made acidic and again alkaline with caustic soda. The precipitate which was of a yellowish colour was again inorganic. The filtrate did not give anything of an alkaloidal nature on extraction with the organic solvents in succession as before. The original extract on concentration and heating with alkali hydroxide, developed ammonia, and it also yielded precipitates with the usual alkaloid reagents. These reactions were evidently due to soluble protein products, since the alkaline liquids, when extracted with either petroleum ether, chloroform or amyl alcohol, yielded nothing of a definite alkaloidal nature.

The fruits contained 7.86 per cent moisture and when completely burnt left 11.41 per cent of a white residue. The ash contained 20.95 % of water soluble and 79.05 % of water insoluble inorganic substances. The ash contained the following

positive and negative radicals:—potassium, calcium, iron, aluminium, magnesium, silicic acid, chloride, phosphate, nitrate and sulphate (the last two in traces).

*Test for enzymes*:—100 g. of the powdered drug was kept in a flask with 300 c.c. distilled water containing 3 c.c. of toluene for 48 hours at room temperature. It was filtered at the pump and the filtrate, which was of a yellow colour, was tested for enzymes.

(i) In each of three test tubes 10 c.c. of one per cent soluble starch solution was kept and to the first tube 10 c.c. enzyme solution, to the second 10 c.c. boiled enzyme solution and to the third 10 c.c. distilled water was added respectively and kept over night. The first tube containing enzyme solution reduced Fehling's solution immediately on slight heating while the other two remained unchanged with the same treatment. This behaviour of the first tube proved the presence of a starch hydrolysing enzyme in the fruits.

(ii) To a cooled (10°C) mixture of 65 c.c. water, 20 c.c. of 5 per cent pyrogallol and 20 c.c. of one per cent hydrogen peroxide was added 10 c.c. of the enzyme solution. In about an hour sufficient quantity of brown precipitate was formed, whereas the control experiments remained unaffected. The precipitate was filtered and was proved to be purpurogallin by its characteristic colour reactions. Thus the fruits contain a peroxidase.

The presence of a peroxidase was also established by adding 10 c.c. enzyme solution to a mixture of 10 c.c. saturated solution of hydroquinone and 10 c.c. 1% hydrogen peroxide, when dark green lustrous slender needles of quinhydrone were formed after about ten minutes. The control experiments remained unaffected. Both the quinhydrone and purpurogallin reactions could not be repeated in the absence of hydrogen peroxide, which shows the absence of oxidase. A detailed study of the peroxidase will be given in a separate communication.

For complete analysis 2 kilogrammes of the powdered fruit were exhaustively extracted with petroleum ether. The extract on complete distillation of the solvent gave 98 g. of a greenish yellow oil of a dark colour. The purification and the constitution of the oil is described separately. The petroleum ether extracted powder was extracted with rectified spirit till the colour of the extract became very light. The extract was brown in colour with a green fluorescence. It was concentrated and the liquid on standing deposited shining white crystals which was identified to be pure potassium chloride and weighed 9.6 g. The filtrate was further concentrated to a volume of about 300 c.c. Water was added and a yellowish-brown paste separated. The filtrate which was a yellowish brown colour gave a yellow precipitate on addition of lead acetate solution. The lead salt was purified and decomposed in aqueous suspension by  $H_2S$ . After removal of the lead sulphide, the mother liquor was evaporated when a brown syrupy mass was obtained. It is constituted mostly of tannins as it gave a greenish-black coloration with neutral ferric chloride solution. The filtrate of the above lead salt gave a second yellow

precipitate with basic lead acetate solution. This precipitate on decomposition with  $H_2S$ , as in the previous case, gave a small quantity brown sticky residue on complete evaporation. It was very soluble in water and reduced Fehling's solution only after being hydrolysed with hydrochloric acid. The substance in alcohol solution developed a purple-violet ring on addition of a few drops of a 20 %  $\alpha$ -naphthol in alcohol and afterwards a layer of concentrated sulphuric acid. This substance is therefore a glucoside; but on account of its not yielding to any of the methods of crystallization, it could not be further investigated.

The pasty precipitate that was obtained by addition of water to the concentrated alcoholic extract was thoroughly washed with water and on standing overnight became brittle and weighed 25g. It was freed from oily contamination with petroleum ether. The product thus obtained was of a brownish yellow colour, contained nitrogen and melted at about  $98^\circ C$ . This on extraction with ether and complete evaporation of the solvent gave a resinous mass having the characteristic odour of the powdered drug. The ether insoluble portion dissolved in alkali and was reprecipitated with the addition of mineral acids. In alcoholic solution it produced a yellow precipitate and also gave a greenish-black coloration with ferric chloride. On boiling with hydrochloric acid a brick red mass was obtained which melted at  $108^\circ C$ . The substance was therefore a phlobaphene.

The alcohol extracted drug was freed from alcohol and was extracted with 2 % cold hydrochloric acid. The filtrate was completely precipitated with excess of Mayer's reagent. The dirty white precipitate was decomposed by  $H_2S$  in alcoholic suspension. The filtrate was freed from  $H_2S$  and on complete evaporation gave yellowish white residue. This substance melted at  $189-91^\circ C$  and on heating evolved ammonia along with a pungent fume of burnt proteins. It also responded to the biuret reaction. This was the substance which gave the precipitates with alkaloidal reagents when the crude drug was extracted with dilute hydrochloric acid.

#### EXAMINATION OF THE OIL

The crude oil was digested with animal charcoal and filtered through a hot filtering funnel. The purified oil was freed from last traces of petroleum ether by heating over water bath and finally in a vacuum desiccator. The oil, which was of a pale yellow colour, on standing overnight deposited a small quantity of white crystalline mass. It was filtered and the precipitate was put on a porous plate. After few days the substance became perfectly white. It was insoluble in cold alcohol but dissolved in it on boiling. The crystallised product melted at  $83^\circ C$ . and weighed 0.17 g. It formed a white lead salt with alcoholic solution of lead acetate and was an aliphatic acid. This substance was confirmed to behenic acid by its lead salt. [Found Pb = 24.2%, behenic acid lead salt  $C_{24}H_{50}O_4Pb$ , requires Pb = 23.4 %]

The oil does not contain nitrogen and sulphur. It is optically active, having a small lævo rotation  $\left[ \alpha \right]_D^{25} = -0.57$ . The fatty acids obtained after saponification of the oil is optically inactive, which shows definitely that the rotation is due to the unsaponifiable matter. The oil burns with a non-sooty, odourless flame and gives a positive reaction for phytosterols. In order to test the drying power of the oil, few drops of it was spread on a clean glass plate and kept at room temperature. After a fortnight the oil became sticky, proving it to be of the class of semi-drying oils. The physical constants of the oil are given in Table I.

Table I.

|                          |     |        |
|--------------------------|-----|--------|
| Specific gravity at 25°C | ... | 0.9148 |
| Refractive index at 20°C | ... | 1.4734 |
| Solidifying point        | ... | 3°C    |
| Acid value               | ... | 42.17  |
| Saponification value     | ... | 184.9  |
| Acetyl value             | ... | 48.03  |
| Iodine value             | ... | 131.3  |
| Unsaponifiable matter    | ... | 1.08   |
| Hehner value             | ... | 96.2   |

Seventy grammes of the oil was subjected to distillation with steam in a 500 c.c. flask. The first 200 c.c. of the distillate was extracted with ether. The ether layer was separated, dried with anhydrous sodium sulphate and on evaporation left no oily residue—proving the absence of volatile oil. The oil was next saponified with alcoholic potash and the unsaponifiable matter was removed with ether in the usual way. The soap solution was dissolved in excess of water and decomposed with dilute sulphuric acid in presence of petroleum ether. The petroleum ether-fatty acid layer was washed free from traces of sulphuric acid in a separating funnel. The mixture of fatty acids was next freed from moisture with anhydrous sodium sulphate, filtered and petroleum ether was distilled off. Table II gives the analytical constants of the fatty acids separated from the oil.

Table II.

|                          |     |        |
|--------------------------|-----|--------|
| Specific gravity at 25°C | ... | 0.8978 |
| Refractive index at 20°C | ... | 1.4721 |
| Iodine value             | ... | 135.6  |
| Neutralisation value     | ... | 187.9  |
| Mean molecular weight    | ... | 298.6  |

The mixture of the fatty acids were then separated into saturated and unsaturated acids by (i) lead-salt-ether method and (ii) Twitchell's lead-alcohol

method. The separation of the saturated and unsaturated acids is more quantitative by the second method as is apparent from the iodine values of the saturated acids. In the experiment with Twitchell's method of separation 20 g. of the fatty acids isolated previously was dissolved in 500 c.c. of 95 per cent ethyl alcohol. The solution was boiled and to it was added a boiling solution of 250 c.c. alcohol containing 13 g. lead acetate. The mixture was kept at room temperature (21°C.) overnight and the precipitated lead salt was filtered and washed free of lead with alcohol. The precipitate was again dissolved in 200 c. c. boiling 95% alcohol containing 1 g. acetic acid and the solution cooled overnight. The precipitate was filtered, purified and decomposed with dilute nitric acid in ethereal solution. The ether solution was washed free of nitric acid, dried and the solid acid was recovered. The mixture of the filtrate of the insoluble lead salt and washings was concentrated to 75 c.c. Water was next added to it and the lead salt was decomposed with dilute nitric acid and the liquid acids isolated as before. Table III gives the percentage of saturated and unsaturated acids as estimated by two methods.

Table III.

|                                   | Percentage of<br>unsaturated acid. | Percentage of<br>saturated acid. | Iodine value of<br>saturated acid. |
|-----------------------------------|------------------------------------|----------------------------------|------------------------------------|
| (i) Lead-salt-ether method ...    | 81'67                              | 18'33                            | 40'62                              |
| (ii) Lead-salt-alcohol method ... | 83'81                              | 16'19                            | 3'08                               |

#### UNSATURATED ACIDS

*Elaidin test for the liquid acid.*—1 g. of the liquid acid was treated with 5 c.c. of nitric acid and 0.6 g. of sodium nitrite was added in small portions and was allowed to stand in a cool place. After some time the acid solidified. The product was next pressed on a porous plate and the resultant solid, when crystallised from ether, melted at 44-45°C. and was identical with elaidic acid.

*Oxidation of the unsaturated acids with potassium permanganate solution.*—10 g. of the acids were oxidised with 2 per cent potassium permanganate in alkaline solution at room temperature with constant stirring. After the reaction a current of sulphur dioxide was passed through the solution to dissolve the precipitated manganese dioxide. The insoluble white substance was filtered and extracted with ether. The ethereal extract, after the removal of the solvent, deposited a product, which on crystallisation from alcohol melted at 134-35°C., and was identified to be dihydroxy-stearic acid. The formation of this acid proved the presence of oleic acid in the liquid acids. The ether insoluble portion of the oxidation product was extracted with boiling water and the filtrate on concentration and cooling deposited crystals, which on drying melted at 164-65°C., and was identified to be tetrahydroxy-stearic acid (sativic acid). The formation of this acid proved the presence of linolic acid in the oil. No hexahydroxy stearic acid could be

isolated from the oxidation product which proved the absence of linolenic acid in the liquid acids.

The iodine value of the mixture of the unsaturated acids was found to be 151.9. Therefore, the proportion of oleic and linolic acids in the unsaturated acids was calculated with the help of the following equations:—

$$X + Y = 100.$$

$$90.07X + 181.14Y = 100 \times I.,$$

where  $X$  = the percentage of oleic acid,

$Y$  = the percentage of linolic acid,

and  $I$  = the iodine value of the mixture of unsaturated acids.

Table IV gives the percentage of oleic and linolic acids calculated from the above equations.

Table IV.

|              |     | Percentage in the<br>unsaturated acids. | Percentage in the<br>total fatty acids. | Percentage in the<br>original oil. |
|--------------|-----|---|---|------------------------------------|
| Oleic acid   | ... | 32.11                                   | 26.91                                   | 25.88                              |
| Linolic acid | ... | 67.89                                   | 56.89                                   | 54.73                              |

The constituents of the unsaturated acids were also estimated by means of their bromine addition products as recommended by Jamieson and Baughmann\*. Accordingly, a known weight of the unsaturated acids was dissolved in 130 c.c. of dry ether and was cooled in a freezing mixture to  $-10^{\circ}\text{C}$ . and dry bromine was added slowly drop by drop till it was in excess. During the addition of bromine, the temperature of the liquid was kept below  $-5^{\circ}\text{C}$  and the mixture was kept for two hours at  $-10^{\circ}\text{C}$ . No precipitate was obtained. The ethereal liquid was then freed from excess of bromine with an aqueous solution of sodium thiosulphate in a separating funnel. The solution was then dried with anhydrous sodium sulphate, filtered and the ether distilled off. The residue was dissolved in 150 c.c. dry petroleum ether with boiling and the flask was put in the ice-chest overnight. The precipitate of the tetrabromo linolic acid was filtered, washed and dried. The filtrate and washings was concentrated to 60 c.c. and again kept in the refrigerator overnight. The second crop of the precipitate was added to the first and weighed. It melted at  $113-14^{\circ}$ . The filtrate was concentrated to 30 c.c. and again kept as before, but this time no precipitate was formed. Finally the petroleum ether was completely removed and the precipitate weighed and its bromine content was determined. The residue on extraction with hot methyl alcohol gave a further quantity of tetrabromo compound. The following table contains the data of the analysis of the bromo derivatives.

Table V.

|  |     |     |                       |
|--|-----|-----|-----------------------|
| Weight of the unsaturated acid taken                   | ... | ... | 4'7347 g.             |
| Linolic acid tetrabromide insoluble in petroleum ether | ... | ... | 3'3784 g.             |
| Residue (dibromide and tetrabromide)                   | ... | ... | 5'8050 g.             |
| Bromine content of the residue                         | ... | ... | 46'2257 %.            |
| Dibromo oleic acid in the residue                      | ... | ... | (41'37%) or 2'4015 g. |
| Tetrabromo linolic acid in the residue                 | ... | ... | (58'63%) or 3'4035 g. |
| Total tetrabromo linolic acid found                    | ... | ... | 6'7819 g.             |
| Linolic acid equivalent to tetrabromide                | ... | ... | 3'1640 g. or 66'83 %. |
| Oleic acid equivalent to dibromide                     | ... | ... | 1'5320 g. or 32'36 %. |

Table VI gives the percentage of oleic and linolic acids in the unsaturated acids as calculated from the above data.

Table VI.

|                  | Percentage in the unsaturated acids. | Percentage in the total fatty acids. | Percentage in the original oil. |
|------------------|--------------------------------------|--------------------------------------|---------------------------------|
| Oleic acid ...   | 32'36                                | 27'12                                | 26'08                           |
| Linolic acid ... | 66'83                                | 56'01                                | 53'88                           |

#### SATURATED ACIDS.

The saturated acids, separated by the lead-salt-alcohol method, was freed from traces of liquid acids by pressing over porous plate. The acid thus obtained melted between 53–56°. It was dissolved in alcohol and precipitated by diluting with water in three instalments; but none of the portion on drying gave definite melting points. The quantity of the saturated acids being too small, it could not be separated into its constituents. Utmost that could be done was to confirm the presence of palmitic and stearic acids by qualitative experiments according to the methods of Kreis and Hafner<sup>5</sup>, and Hehner and Mitchell.<sup>6</sup>

My best thanks are due to Dr. S. Dutt for the kind interest he has taken in the work and to the 'Kanta Prasad Research Trust' of the Allahabad University for a scholarship which enabled me take part in the investigation.

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## PEROXYDASE FROM THE FRUITS OF *TRIBULUS TERRESTRIS*, LINN.

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In a previous communication,<sup>1</sup> on the chemical examination of the fruits of *Tribulus terrestris*, or *Chota Gokhru* as it is known in Hindi and small caltrops in English, a reference was made of the presence of a good quantity of peroxydase in the fruits. The fact that the fruits are widely used as a good tonic and blood purifier interested the present authors for a detailed and systematic study of the enzyme which is most probably responsible for the alleged physiological properties of the drug. The fruits of the plant are found to be a good source for the enzyme. The plant grows in abundance in the waste sandy soil throughout India. The present paper deals with the various factors affecting the activity of the peroxydase of the extract prepared from the crushed fresh fruits of the plant.

### Experimental

Fresh fruits of *Tribulus terrestris* were washed and crushed well in a porcelain mortar and 500 g. of the crushed material with 1500 c.c. of distilled water and few c.c. of toluene were kept in a big flask for a day in the 'Frigidaire'. The pulp was first cloth filtered and next transferred to a hand-screw press, and the sap expressed as completely as possible by applying pressure. The filtered and expressed solution thus obtained amounted to 1600 c.c. The extract was then filtered through

paper pulp into a Jena glass bottle, toluene was added and kept in the refrigerator at 0°C. The activity of the solution remained unchanged even after three weeks.

A portion of the extract was dialysed through a parchment bag in a tall beaker at 15°C for five days against distilled water to which toluene had been added. The water was frequently replaced every day. After dialysis the solution was filtered to free it from suspended impurities into a Jena glass bottle containing toluene and preserved in the refrigerator. An extract prepared in this way retained its activity for a long time.

The peroxylase activities were determined by a method based on that described by Luther and Leubner<sup>2</sup> and Dey and Sitharaman<sup>3</sup>. The method briefly consists in precipitating and filtering the quinhydrone formed when the peroxylase acts on hydroquinone in presence of hydrogen peroxide, dissolving the precipitate in alcohol and titrating the iodine liberated with standard thiosulphate when a mixture of alcohol (20 c.c. 95%), concentrated hydrochloric acid (20 c.c.) and potassium iodide (20 c.c. of 10%) was added to the alcoholic extract of the quinhydrone.

The activities are always expressed in terms of c. c. of N/10 thiosulphate.

It is interesting to note that the activity of the peroxylase was not impaired on dialysis for five days. 200 c. c. of the extract was dialysed for five days and the volume was made up to 800 c.c. This was again diluted with its own volume of water for the estimation of peroxylase activity in all the subsequent experiments. A similar extract was kept at the same temperature and diluted to the same extent and finally the activities of both the dialysed and undialysed extracts were compared.

To 10 c.c. of Walpole's acetate buffer of  $P_H$  5.3 was added 0.4 g. of hydroquinone and 10 c.c. of 2% by volume of  $H_2O_2$  and finally 10 c.c. of the enzyme solution (total volume 40 c.c.). The reaction was carried at 15°C. for 15 minutes, and was stopped by adding 3 c.c. of 2N-HCl.

|                      | Activity in terms of c.c.<br>of N/10 thiosulphate. |
|----------------------|--|
| Dialysed solution,   | 10.80; 10.95.                                      |
| Undialysed solution, | 11.50; 11.65.                                      |

### Effect of Concentration of the Peroxylase on its Activity.

Since the extract was found to contain peroxylase in very concentrated form, it was necessary to choose a proper concentration of the enzyme, in order to study the course of the reaction of the enzyme on the substrate. Experiments were, therefore, carried out with extracts containing varying amounts of the enzyme. The reaction mixture consisted of 0.4 g. of hydroquinone, 10 c.c. of 2 per cent by volume of hydrogen peroxide and 10 c.c. of undialysed enzyme solution (Total volume 30 c.c.). The reaction was carried at 15°C. and was stopped by the

addition of 3 c.c. of 2 N-HCl at required intervals. The results have been presented in Table I and Fig. I.

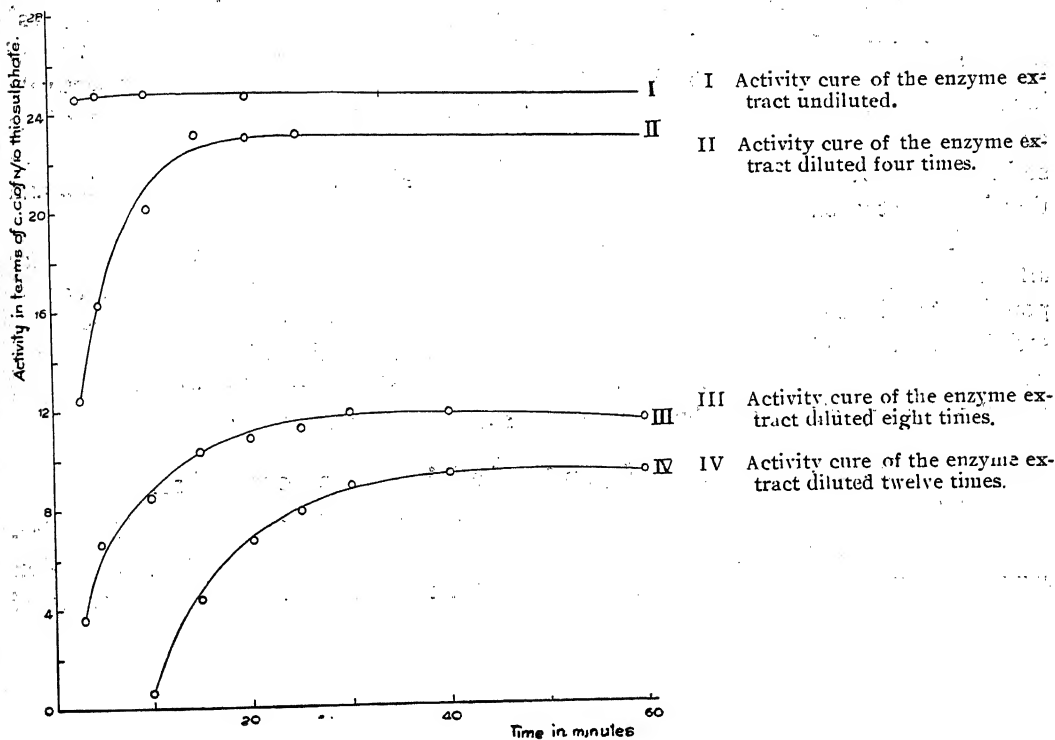


Fig. 1

Table 1.

| Time in minutes           | ... | 3     | 5     | 10    | 15    | 20    | 25    | 30    | 40    | 6.0   |
|---------------------------|-----|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| N/10 Thiosulphate in c.c. |     |       |       |       |       |       |       |       |       |       |
| Undiluted extract         | ... | 24.05 | 24.75 | 24.70 | ...   | 24.65 | ...   | ...   | ...   | ...   |
| Diluted four times        | ... | 12.40 | 16.20 | 20.15 | 23.05 | 22.95 | 23.00 | ...   | ...   | ...   |
| Diluted eight times       | ... | 3.55  | 6.60  | 8.55  | 10.30 | 10.80 | 11.20 | 11.80 | 11.80 | 11.45 |
| Diluted twelve times      | ... | ...   | ...   | 0.55  | 4.30  | 6.80  | 7.85  | 8.85  | 9.30  | 9.50  |

In Fig. I the series of curves represent the increase in the amount of quinone formed, as measured by c.c. of thiosulphate, in hydroquinone solution under the action of various relative amounts of the same enzyme solution. Several things are to be noticed in these curves. These curves indicate in a general way the rate of change at the earlier stage of the reaction is proportional to the concentration of the enzyme, as is seen in the relative steepness of the curves. It may be noted that the curves II, III and IV do not reach to such a height as that of the curve I. This is due to the destruction of the enzyme in the course of its action on the substrate. In the experiments of Herzog and Meier\* similar observations were made. They noticed that there is a relationship between the amount of oxidation brought about by a given quantity of hydrogen peroxide. This is attributed to the

destructive action of the peroxide on the enzyme, since the latter was found to be absent at the end of the reaction, when small amounts were added. Similar behaviour was observed of other enzymes with regard to the final result. Bayliss<sup>5</sup> has observed in the case of trypsin that the enzyme is destroyed in the course of its action on the substrate, when the concentration of the enzyme is selectively low. Some enzymes, however, withstand the destruction in the course of its action on the substrate and remains unaltered at the end of the reaction. Starkenstein<sup>6</sup> has shown that amylase remains unaltered at the end of the reaction and that it can act upon a further supply of substrate.

The enzyme concentration corresponding to the curve III was chosen for all other experiments since it can be found from the results that a dilution corresponding to  $\frac{1}{8}$ th of the enzyme concentration of the undiluted extract works most satisfactorily. A 15 minutes reaction period and 10 c.c. of the diluted enzyme which was found to be most suitable under the conditions of our experiments were chosen for all other experiments. The reaction was always carried at 15°C.

### The influence of $P_H$ Upon the Activity of the Peroxydase.

The reaction mixture consisted of 0.4 g. of hydroquinone, 10 c.c. of 2% hydrogen peroxide, 10 c.c. of enzyme solution and 10 c.c. of buffer of varying hydrogen-ion concentrations (total volume 40 c.c.). Walpole's acetate buffer, providing a range of

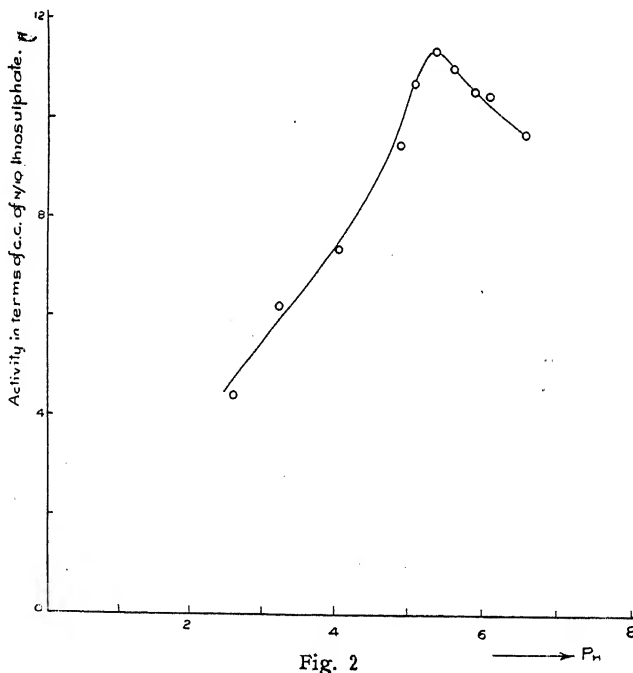


Fig. 2

$P_H$  2.6 to  $P_H$  6.5 was used to maintain the  $P_H$  of the medium. The reaction was carried at 15°C. for 15 minutes and stopped by adding 3 c.c. of 2 N-HCl.

The results are presented in Table II and Fig. II.

Table II.

| pH                         | ... | 2.6  | 3.2  | 4.0  | 4.8  | 5.0   | 5.3   | 5.5   | 5.8   | 6.0   | 6.5  |
|----------------------------|-----|------|------|------|------|-------|-------|-------|-------|-------|------|
| N/10 thiosulphate in c. c. |     | 4.50 | 6.30 | 7.45 | 9.60 | 10.80 | 11.50 | 11.15 | 10.70 | 10.65 | 9.85 |

The results indicate that the maximum activity of the peroxydase lies between pH 5.3 and 5.5 in the acid region.

### Effect of hydrogen peroxide concentration on peroxydase activity

Bach<sup>7</sup>, Willstater and Weber<sup>8</sup>, Mann<sup>9</sup>, Dey and Sitharaman<sup>3</sup> have shown that excess of hydrogen peroxide inhibits the activity of peroxydases. It was, therefore, necessary to determine the proper concentration of hydrogen peroxide to be employed in each experiment.

Several experiments were made in which the concentration of hydrogen peroxide was varied, while all other factors were kept constant. The reaction mixture consisted of 0.4 g. of hydroquinone, 10 c. c. of buffer (pH 5.3), 10 c. c. of hydrogen peroxide of varying concentrations and 10 c.c. of the enzyme solution

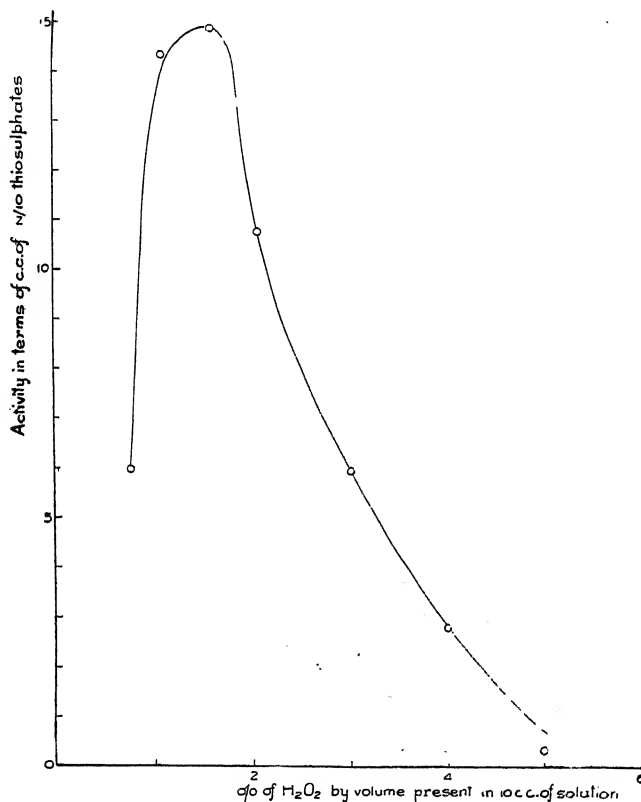


Fig. 3

(Total volume 40 c. c.) The reaction was carried for 15 minutes at 15°C. The results are given in Table III and Fig. III.

Table III.

|  |     |      |      |      |       |       |       |      |     |
|--|-----|------|------|------|-------|-------|-------|------|-----|
| Percentage by volume of $H_2O_2$<br>in 10 c.c. ... | 7.5 | 5.0  | 4.0  | 3.0  | 2.0   | 1.5   | 1.0   | .75  | 0.5 |
| N/10 thiosulphate in c. c. ...                     | ... | 0.35 | 2.80 | 5.95 | 10.75 | 14.85 | 14.30 | 5.90 | ... |

It can thus be seen that under the conditions of our experiments, the maximum activity is attained with 1.5 per cent of hydrogen peroxide.

#### Effect of concentration of Substrate upon the action of the peroxydase

A series of flasks containing 10 c.c. of hydrogen peroxide (1.5%), 10 c.c. of buffer (PH 5.3), 10 c.c. of enzyme solution and hydroquinone of varying concentrations in 10 c.c. were taken and reactions were carried for 15 minutes at 15 C. The results are presented in Table IV and Fig IV.

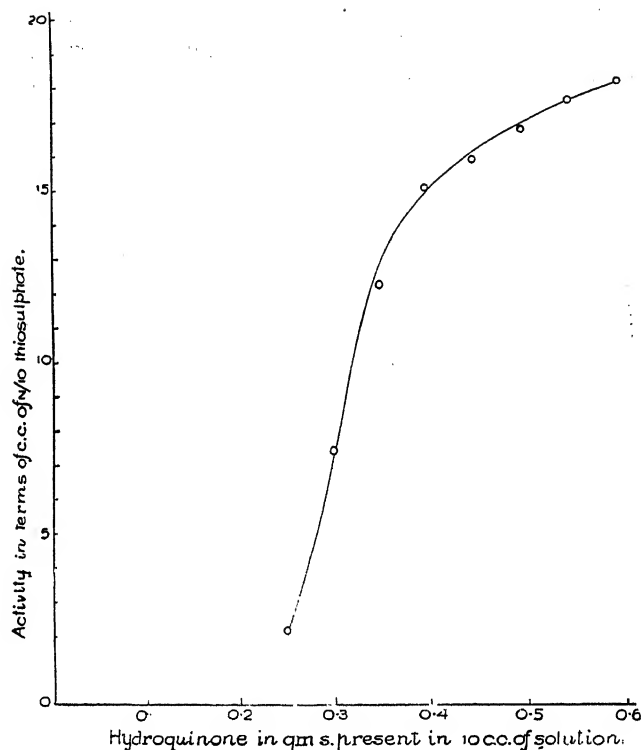


Fig. 4

Table IV.

|  |       |       |       |       |       |       |      |      |     |
|--|-------|-------|-------|-------|-------|-------|------|------|-----|
| Wt. of Hydroquinone in gram<br>in 10 c.c. of water ... | .60   | .55   | .50   | .45   | .40   | .35   | .30  | .25  | .20 |
| N/10 thiosulphate in c.c. ...                          | 18.05 | 17.50 | 16.70 | 15.80 | 15.00 | 12.20 | 7.45 | 2.05 | ... |

The curve in Fig IV shows that the activity of the enzyme is increased with the increase in concentration of the substrate. At higher concentrations, however, the change in the activity of the enzyme, with the change

in the concentration of the substrate, is not so great as it is at lower concentrations of the substrate. Getchell and Walton,<sup>10</sup> however, have shown that in the case of the peroxydase of horse-radish there is an optimum concentration of maximum activity and on further increase in the concentration of the substrate pyrogallol, the activity of the enzyme tends to decrease. Dey and Sitharaman<sup>3</sup> have also made similar observations with the peroxydase of *Chow Chow*. They have shown that the activity of the peroxydase remains constant when the concentration of the substrate is between 0.25 and 0.35 at the total volume of 13 c.c.

#### **Influence of temperature on the stability of the peroxydase**

Most of the enzymes in solution are inactivated at a temperature above 45°C. But enzymes differ in their thermostability. Some proteolytic enzymes and peroxydases can resist even 100°C, for a short period.<sup>11</sup> Experiments were, therefore, carried to determine the heat stability of the peroxydase under investigation.

Enzyme solutions were kept for 40 minutes at different temperatures in a thermostat and the activities were determined by taking out 10 c.c. of the enzyme solution and adding to the reaction mixture, which consisted of 0.4 g. of hydroquinone, 10 c.c. of hydrogen peroxide (1.5%), 10 c.c. of buffer (pH 5.3), and the volume

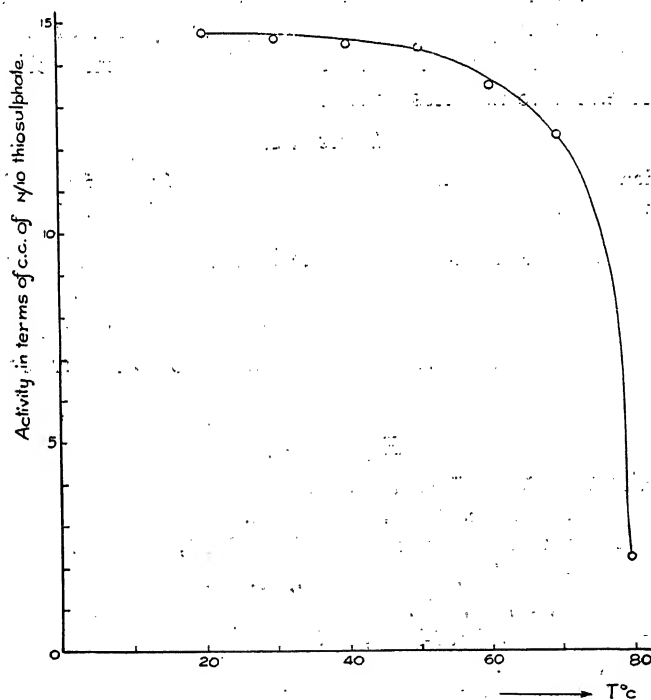


Fig 5

made up to 30 c.c. The time and temperature of the reaction were kept constant as in previous experiments. The results have been presented in Table V and Fig. V.

Table V.

| Temperature at which the enzyme<br>Solution was kept for 40 minutes ... | 20°   | 30°   | 40°   | 50°   | 60°   | 70°   | 80°  |
|---|-------|-------|-------|-------|-------|-------|------|
| N/10 Thiosulphate in c.c. ...   | 14.80 | 14.65 | 14.50 | 14.50 | 13.65 | 12.50 | 2.30 |

It may be noted that up to 50°C, the enzyme is very stable and from 60°C. the inactivation of the enzyme begins to increase considerably, as the temperature is increased, and finally the activity of the enzyme is almost nil when it is kept at 80°C. These results indicate that the enzyme peroxidase is very stable at temperatures below 50°C.

#### Stability of the peroxidase at 75°C at different hydrogen-ion concentrations.

It is well known that the reaction of the medium greatly influences the thermostability of an enzyme. Experiments were, therefore, conducted with a view to know the range of the hydrogen-ion concentration of the medium, at which the enzyme peroxidase is most stable.

The inactivation experiments were carried out by putting 20 c.c. of the enzyme solution (original solution diluted four times) in different flasks with 20 c.c. of buffers of different pH and keeping the flasks at 75°C. for 30 minutes and finally estimating the activity. The results are presented in Table VI.

The reaction mixture for estimating the activity constituted of 20 c.c. of Walpole's acetate buffer (pH 5.3), 0.4 g. of hydroquinone, 1 c.c. of hydrogen peroxide (15%) and 10 c.c. of the inactivated enzyme solution. (Total volume 41 c.c.) The reaction was carried for 15 minutes at 15°C.

Table VI.

|                               |     |     |     |      |      |     |     |     |
|-------------------------------|-----|-----|-----|------|------|-----|-----|-----|
| pH of inactivation ...        | ... | ... | ... | 6.5  | 5.3  | 4.8 | 4.0 | 3.2 |
| N/10 Thiosulphate in c.c. ... | ... | ... | ... | 5.60 | 0.25 | ... | ... | ... |

The results indicate that the enzyme is unstable at the more acid region of the medium.

Further work on the purification of the enzyme is in progress.

Our thanks are due to Prof. N. R. Dhar and Dr. S. Dutt for their kind interest in the work.

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# STUDIES ON THE EFFECT OF PHOSPHATES ON RESPIRATION OF GREEN LEAVES 1. EUGENIA JAMBOLANA, 2. ALLIUM TUBEROSUM

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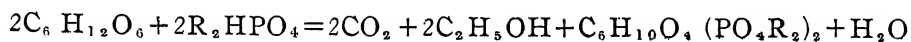
Communicated by Prof. J. H. Mitter.

Received January 11, 1933

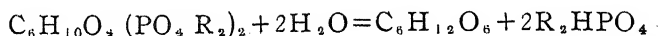
## INTRODUCTION

That plants and plant-tissues give out carbon-dioxide even in absence of oxygen has long been known. And it has been accepted that the chemical reaction by which this carbon-dioxide is produced is the same as that of the alcoholic fermentation of sugar. The decomposition of respirable sugars within plant cells into alcohol and carbon-dioxide is looked upon as a vital phenomenon in as much as the early stages are common in both the anaerobic and aerobic forms of respiration, down to the formation of the immediately oxidisable basic substance, its fate and the nature of respiratory wastes being determined by the presence or absence of oxygen.

The works of Harden and Young are of special interest in connection with the alcoholic fermentation of sugars. They found that the rate of fermentation is greatly accelerated by adding boiled yeast juice to the fermenting solution. "The accelerating factor is a phosphate." Thus the alcoholic fermentation of glucose involves two definite stages, the primary stage being the production of hexose phosphates :—



In the second stage this hexose phosphate is hydrolysed, when the free phosphate is set free to combine with glucose again, the hydrolysis being brought about by an enzyme, hexose-phosphatase:—



Thus phosphates which are vitally connected with alcoholic fermentation and accelerates its rate might also have a similar effect on the aerobic phase of respiration in view of what has been said before.

Iwanoff showed that phosphates exert an accelerating effect upon respiration which is related to alcoholic fermentation. Zaleski and Reinhard have found out that "these salts accelerate both the anaerobic and the oxidation phase of respiratory process."

Lyon worked on *Elodea canadensis* and wheat seedlings and has come to the conclusion that "phosphate increases the rate of production of  $CO_2$  by anaerobic processes because of its role in the early stages of alcoholic fermentation. It effects an increase in the production of  $CO_2$  by the aerobic phase of respiration through its action as a catalyst toward oxidases."

In this paper an attempt has been made to study the effects of injection of soluble neutral phosphates and phosphate-sugar solutions into leaves of tropical plants on their aerobic and anaerobic respiration and their sugar contents.

#### MATERIALS AND METHOD

Leaves were the only organs selected for this work. This was so because foliage organs are best suited for a study of respiration and sugar content, these being the centre of carbohydrate formations. The materials were collected from these plants:—

(1) *Eugenia jambolana*, and (2) *Allium tuberosum*. These were selected especially because much work on the physiology of these leaves has already been done in this laboratory and also because these leaves yield themselves to injection very easily. The phosphate used throughout the work was neutral Potassium phosphate. The leaves were injected either with one per cent solution of Potassium phosphate or with a mixture of 1 gm. potassium phosphate plus 1 gm. sugar (glucose or sucrose) dissolved in 100 c.c. of distilled water. Neutral phosphate was made in this way: two 5 % solutions were prepared, one of alkaline potassium phosphate ( $K_2HPO_4$ ) and the other of acid potassium phosphate ( $KH_2PO_4$ ). These were titrated against each other. From the amount of solutions used the number of grams of each salt was calculated. From the result obtained it was found out how much of each salt would be contained in one gram of neutral mixture.

A vacuum pump was used for injection. For this purpose the leaves were put in a large test tube, which was filled with water or the solution as needed,

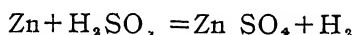
and was connected with the pump. Then, by working the pump and then releasing the pressure the leaves got injected.

For measuring respiration the following Apparatus was used.

A thermostat bath was maintained at a constant temperature, *viz.*, 34°C-35°C. In it were kept the leaf chambers, which were moderately wide glass cylinders open at one end. The open end was fitted with a rubber stopper carrying two glass tubes bent at right angles, one was connected with the air commutator and the other with a bottle filled with strong potassium hydroxide solution to absorb carbon dioxide from the ingoing air-current. The Blackman's air commutator is so well-known that it need not be described at length. It is a device by which the respiratory current is automatically shifted on to the next Pettenkoffer tube after some fixed interval of time. This interval was three hours in the present case. The commutator was connected to Pettenkoffer tubes which in their turn were joined to large drums, filled with water, to serve as aspirators. The aspirators dropped at a uniform rate of about 1000 c.c. of water per hour, thus drawing in a slow and constant current.

The content of each Pettenkoffer tube was poured out, after the regular respiratory current had passed through it, and titrated with standard hydrochloric acid. The amount of carbon dioxide absorbed was calculated from the difference in the quantity of hydrochloric acid used to neutralise this and 25 c.c. of baryta directly.

For anaerobic current, wherever it was required, hydrogen, instead of nitrogen, was used. A Kipp's apparatus was utilized for this purpose. Pure zinc granules (free from arsenic) and pure diluted sulphuric acid (with a few crystals of pure copper sulphate) were used:—



The hydrogen thus evolved was made to pass through pyrogallic acid before it entered the plant chambers.

For sugar estimations the leaves were weighed out and then boiled in water to kill the enzymes. The pieces were then thoroughly crushed with clean sand, and then the paste was thoroughly mixed with the same water which was used to kill the enzymes. The whole mass was then pressed through a thin cloth and the liquid thus obtained was filtered by means of a Buchner Funnel. Lead acetate was added to the filtrate for precipitating tannin. The extra amount of lead in the filtrate was got rid of by repeatedly passing hydrogen sulphide. The surplus amount of hydrogen sulphide was boiled off. The volume of solution was measured and the amount of sugar was estimated by titrating against Pavy's solution.

For the estimation of the disaccharides a known volume of the leaf extract was previously boiled with 1 c.c. of conc. hydrochloric acid and then neutralised with sodium bicarbonate. The difference between the results obtained with

hydrolysed and unhydrolysed leaf-extracts multiplied by '95 gives the amount of disaccharides.

### RESULTS AND GENERAL DISCUSSION

I. *The comparison of  $CO_2$  values obtained in air.*—For the purpose of general discussion it would be better to take up the curves in air and in hydrogen separately. Fig. 1 shows the respiratory curves of *Eugenia jambolana* in air

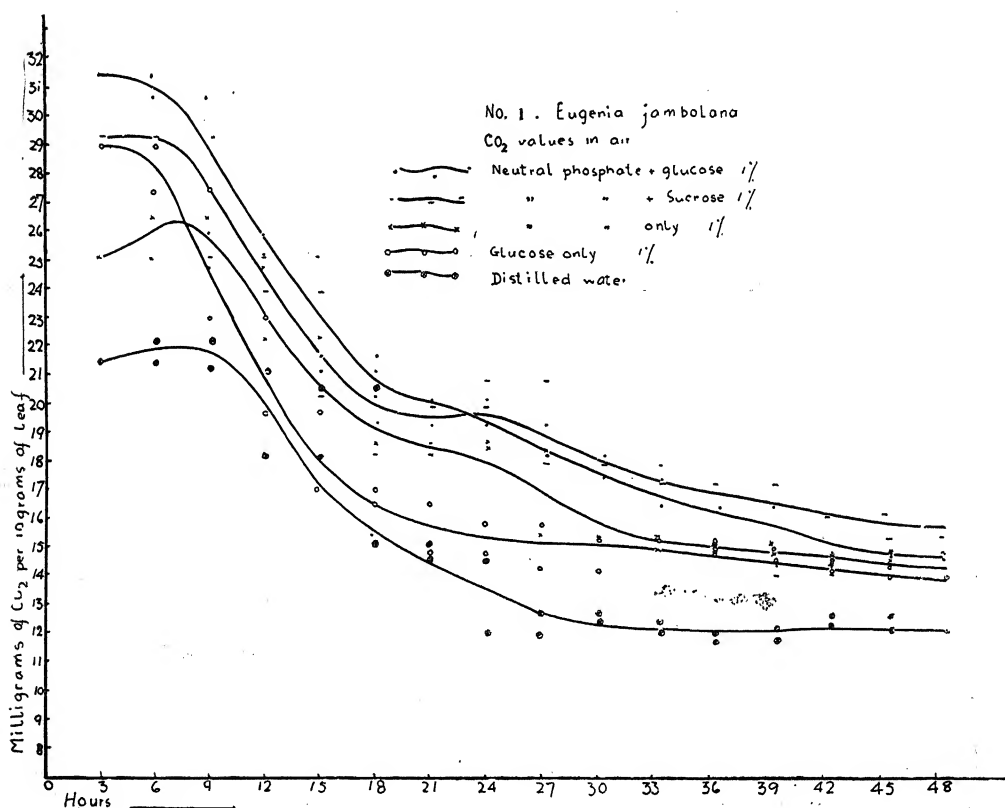


Fig. 1

An Examination of this figure will reveal the fact that the respiration of the water-injected leaves is lowest of all, above it comes that of the glucose-injected ones, then comes the phosphate-line, and then above all are the phosphate-sugar curves.

A similar figure (Fig. 2) in the case of *Allium* leaves reveals the same facts, starting from the lowest to the highest the various curves are in the following

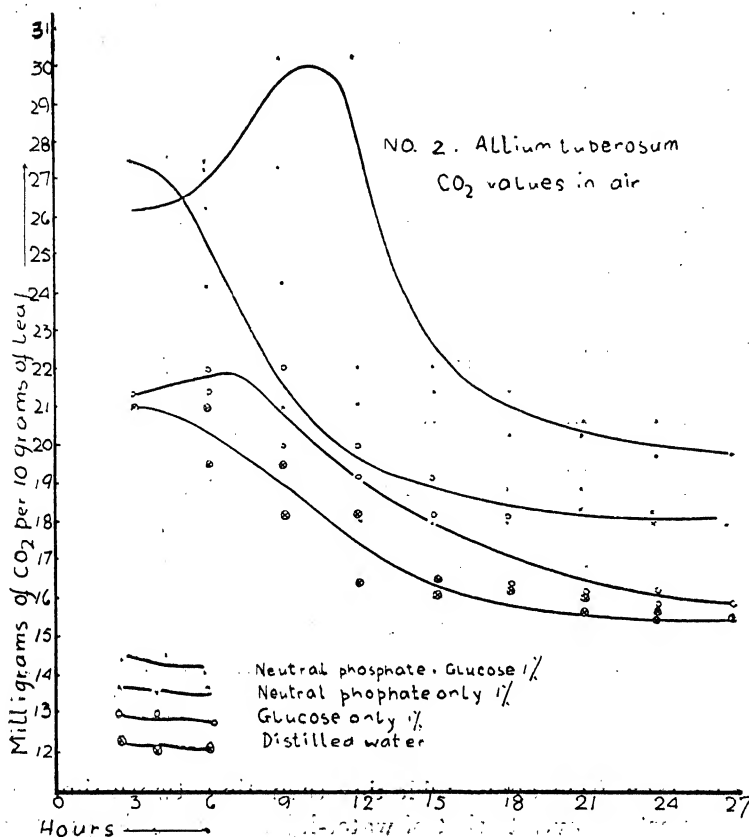


Fig. 2

order—water-line, glucose-line, phosphate-line and finally the phosphate-glucose line.

It would be profitable to find out some relation between the respiratory intensities of the variously injected leaves so that they may directly comparable with reference to same standard. For this purpose the CO<sub>2</sub> value of the water-injected leaves has been taken as a standard and the respiratory values of the differently-treated leaves have been referred to it. The following table (No. 1) gives the approximate ratio obtained in this way.

Table 1

| Treatment of leaves.             | Time     | Mgs CO <sub>2</sub> given out. | Ratio (approximate). |
|----------------------------------|----------|--------------------------------|----------------------|
| <i>Eugenia jambolana</i> ...     | ...      | ...                            | ...                  |
| Glucose injected ...             | ...      | 265.0                          |                      |
| Water injected ...               | 45 hours | 228.7                          | 1.15                 |
| Phosphate injected ...           | ...      | 277.8                          |                      |
| Water injected ...               | 45 hours | 228.7                          | 1.22                 |
| Phosphate + glucose injected ... | ...      | 304.1                          |                      |
| Water injected ...               | 45 hours | 228.7                          | 1.33                 |
| Phosphate + sucrose injected ... | ...      | 304.1                          |                      |
| Water injected ...               | 45 hours | 228.7                          | 1.32                 |
| <i>Allium tuberosum</i> ...      | ...      | ...                            | ...                  |
| Glucose injected ...             | ...      | 149.0                          |                      |
| Water injected ...               | 24 hours | 137.9                          | 1.08                 |
| Phosphate injected ...           | ...      | 163.8                          |                      |
| Water injected ...               | 24 hours | 137.9                          | 1.2                  |
| Phosphate + glucose injected ... | ...      | 187.3                          |                      |
| Water injected ...               | 24 hours | 137.9                          | 1.36                 |

It will be seen from above table that the ratio between the CO<sub>2</sub> output of phosphate-sugar injected leaves to that of water-injected ones is greater than the ratio obtained in the cases of others.

II. *The comparison of CO<sub>2</sub> values obtained anaerobically.*—When the leaves, similarly injected as the above are subjected to hydrogen-treatment for some time, the CO<sub>2</sub> values, thus obtained anaerobically, stand in the same gradation as that obtained in air. Figs. 3 (*Eugenia jambolana*) and 4 (*Allium tuberosum*) will make it clear. It will be seen that the CO<sub>2</sub> output of the water-injected leaves is lowest of all, higher than this comes that of the glucose-injected ones, the phosphate-line follows next and highest is the phosphate-sugar-line.

The following table (No. 2) gives the relation of the CO<sub>2</sub> values of the leaves treated differently with reference to the CO<sub>2</sub> output in the case of water-injected leaves, in anaerobic treatment.

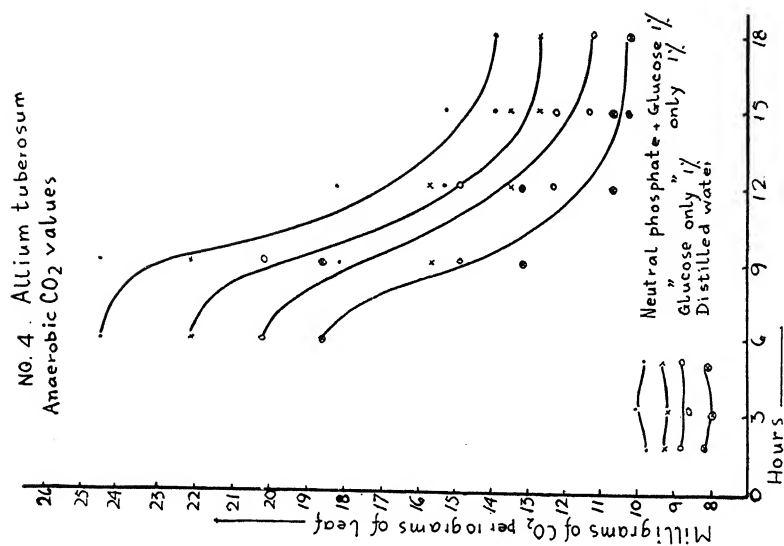


Fig. 4

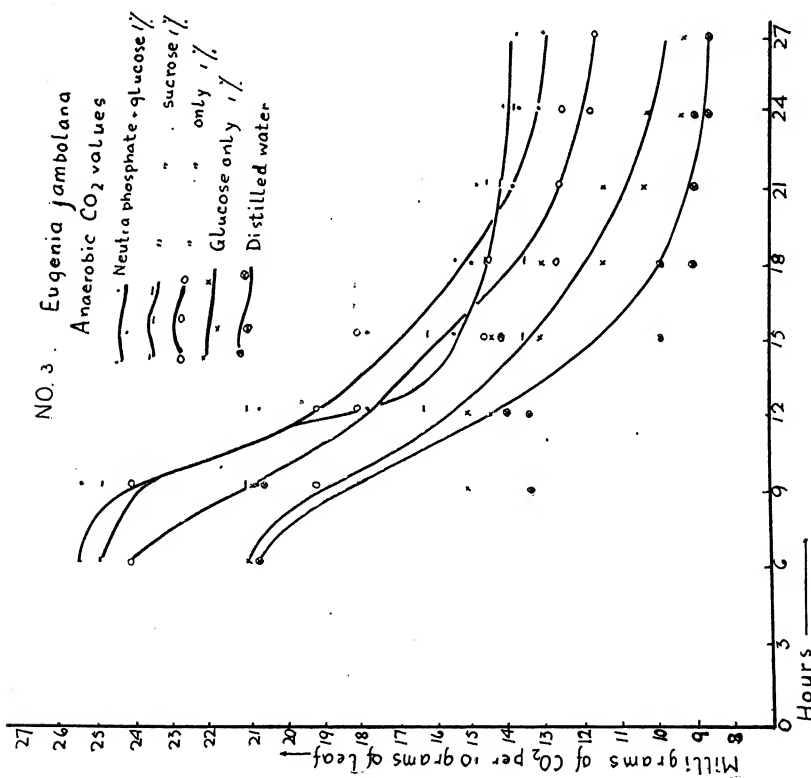


Fig. 3

Table 2

| Treatment of leaves.           | Time.    | Mgs. CO <sub>2</sub> given out. | Ratio (approximate). |
|--------------------------------|----------|---------------------------------|----------------------|
| <i>Eugenia jambolana</i> ...   | ...      | ...                             | ...                  |
| Glucose injected ...           | ...      | 95.7                            | ...                  |
| Water injected ...             | 21 hours | 84.3                            | 1.13                 |
| Phosphate injected ...         | ...      | 113.1                           | ...                  |
| Water injected ...             | 21 hours | 84.3                            | 1.34                 |
| Phosphate+glucose injected ..  | ...      | 121.2                           | ...                  |
| Water injected ...             | 21 hours | 84.3                            | 1.44                 |
| Phosphate+sucrose injected ... | ...      | 118.2                           | ...                  |
| Water injected ...             | 21 hours | 84.3                            | 1.4                  |
| <i>Allium tuberosum</i> ...    | ...      | ...                             | ...                  |
| Glucose injected ...           | ...      | 58.6                            | ...                  |
| Water injected ...             | 12 hours | 52.3                            | 1.1                  |
| Phosphate injected ...         | ...      | 63.8                            | ...                  |
| Water injected ...             | 12 hours | 52.3                            | 1.22                 |
| Phosphate+glucose injected ... | ...      | 71.7                            | ...                  |
| Water injected ...             | 12 hours | 52.3                            | 1.37                 |

The ratio between the CO<sub>2</sub> output phosphate-sugar injected leaves and that of water-injected leaves is thus seen to be the greatest. Below this comes the ratio between the CO<sub>2</sub> values of phosphate injected and water injected leaves and finally the lowest of all is the ratio of glucose and water-injected leaves. If a comparison is made between these figures and those obtained from CO<sub>2</sub> values in air (given in table No. 1) it will be seen that they are almost the same in both the cases, those of *Eugenia jambolana* being very slightly higher in case of anaerobic treatment. But on the whole the results obtained here are similar to those obtained in air.

III. *Comparative study of the "after-effect"*.—Temporary anaerobiosis is generally accompanied by a rise of the CO<sub>2</sub> value, when aerobic conditions are restored. Here also when the leaves, respiring in hydrogen, were brought back to air a huge extra amount of CO<sub>2</sub> was produced before the CO<sub>2</sub> output became steady once again. The following figure (No. 5) offers a comparative study of the after-effects of the variously treated leaves in the case of *Eugenia jambolana*. It is evident from the figure that the water-injected leaves have the lowest after-effect; above this is that of glucose-injected leaves. The highest after-effects are those given by Phosphate-sugar-injected leaves and below this is the phosphate hump. In the following table (No. 3) are given the ratio



between the total CO<sub>2</sub> output of leaves, variously treated, with that of water-injected ones, after the restoration of air current:

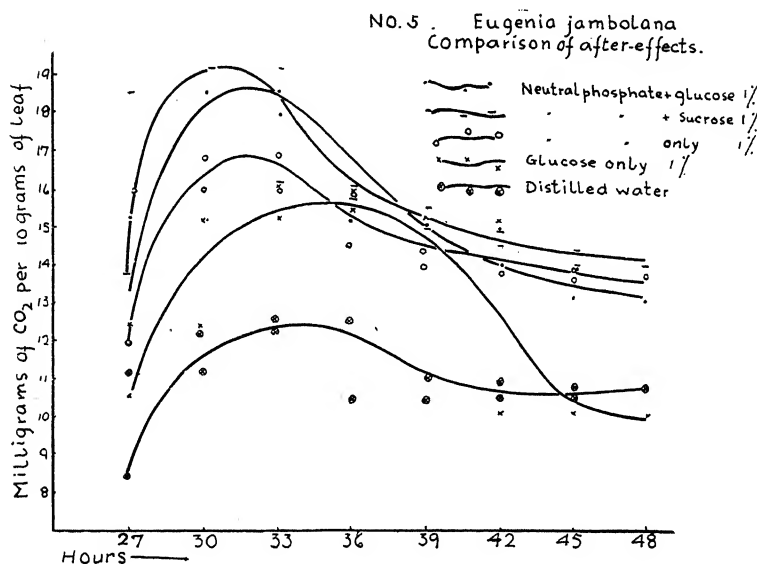


Fig. 5

Thus the Phosphate-sugar injected leaves give the highest ratio, below this come the phosphate-injected leaves, and lowest of all the sugar-injected ones. A comparison of these figures with those calculated from the CO<sub>2</sub> values of leaves respiring in air throughout, will correspond that they reveal with each other, although the ratio in the case of after-effects are a little higher.

Table 3

| Treatment of leaves.             | Time.    | Mgs. CO <sub>2</sub> given out. | Ratio (approximate). |
|----------------------------------|----------|---------------------------------|----------------------|
| Glucose injected ... ..          | 21 hours | 94.9                            | 1.2                  |
| Water injected ... ..            |          | 78.6                            |                      |
| Phosphate injected ... ..        | 21 hours | 104.8                           | 1.33                 |
| Water injected ... ..            |          | 78.6                            |                      |
| Phosphate + glucose injected ... | 21 hours | 107.6                           | 1.4                  |
| Water injected ... ..            |          | 78.6                            |                      |
| Phosphate + sucrose injected ... | 21 hours | 113.7                           | 1.44                 |
| Water injected ... ..            |          | 78.6                            |                      |

But the same condition of things do not exactly obtain in the case of *Allium tuberosum* leaves as will be clear from the following table (No. 4). Here the last two figures are the same, but in the case of aerobic conditions, dealt with previously, the ratio between the CO<sub>2</sub> value of phosphate-glucose-injected leaves

Table 4

| Treatment of leaves.      | Time.    | Mgs. CO <sub>2</sub> given out. | Ratio (approximate). |
|---------------------------|----------|---------------------------------|----------------------|
| Glucose injected ... ..   | 12 hours | 46.0                            | 1.02                 |
| Water injected ... ..     |          | 44.9                            |                      |
| Phosphate injected ... .. | 12 hours | 52.6                            | 1.17                 |
| Water injected ... ..     |          | 44.9                            |                      |
| Phosphate+glucose ... ..  | 12 hours | 52.4                            | 1.17                 |
| Water injected ... ..     |          | 44.9                            |                      |

and that of water-injected leaves was higher. Such a coincidence of figures as has been obtained here, may be taken as accidental.

IV. *The effect on sugar-content in the case of respiration in air.*—Sugar estimations were done in many cases before and after the experiments. From these the amount of sugar utilized during respiration was found out. It would be profitable to compare the sugar values of leaves that were given phosphate, either alone or in a mixture, with those that were not given phosphate at all. This is shown in the following table (No. 5).

Table 5

| Treatment of leaves.                  | Mgs. Monosaccharides consumed per 10 grams. | Mgs. Disaccharides consumed per 10 grams. |
|---------------------------------------|---|---|
| <i>Eugenia jambolana</i> ... ..       |   |   |
| Exp. 1. { A. Phosphate only ... ..    | 79  | 31  |
| { B. Water only ... ..                | 65  | 26  |
| Exp. 3. { A. Phosphate+glucose ... .. | 69  | 34  |
| { B. Glucose only ... ..              | 59  | 29  |
| <i>Allium tuberosum</i> ... ..        |   |   |
| Exp. 7. { A. Phosphate only ... ..    | 80  | 30  |
| { B. Water only ... ..                | 73  | 24  |
| Exp. 9. { A. Phosphate+glucose ... .. | 85  | 21  |
| { B. Glucose only ... ..              | 72  | 19  |

Thus it will at once be evident that more sugar, both monosaccharides and disaccharides, has been consumed, during respiration, in those leaves in which either phosphate or a mixture of phosphate and glucose has been injected.

A similar consumption of more sugar by the leaves injected with phosphate is also manifested in experiments in which they were treated anaerobically, as will be observed from the following table (No. 6).

Table 6

| Treatment of leaves. |                      |     | Mgs. Monosaccharides<br>consumed per 10 grams. | Mgs. Disaccharides<br>consumed per 10 grams. |
|----------------------|----------------------|-----|--|--|
| Eugenia jambolana    | ...                  | ... |  |  |
| Exp. 2.              | A. Phosphate only    | ... | 91   | 41   |
|                      | B. Water only        | ... | 84   | 34   |
| Exp. 4.              | A. Phosphate+glucose | ... | 72   | 35   |
|                      | B. Glucose only      | ... | 58   | 31.1   |
| Allium tuberosum     | ...                  | ... |  |  |
| Exp. 8.              | A. Phosphate only    | ... | 85   | 27   |
|                      | B. Water only        | ... | 79   | 22   |
| Exp. 10.             | A. Phosphate+glucose | ... | 93   | 32   |
|                      | B. Glucose only      | ... | 86   | 30   |

V. *Effect of phosphate on starved leaves.*—This greater consumption of sugar in the phosphate-injected leaves is compatible with their higher respiration level. A glance at the figures (1 and 2) will bring out the fact that the differences between the various curves tend to decrease towards the latter hours of the experiment. Thus the initial differences between the curves are far greater than the final differences. This may be taken to mean that the differences tend to minimise as the store of respirable matter becomes more and more exhausted, *i.e.*, the decrease in the sugar content of the leaves, possibly, modifies the effect of the phosphate on their respiration. Of special interest in this connection is the following figure. Here the leaves (of *Eugenia jambolana*) were injected with phosphate after 21 hours starvation, by which time their sugar content decreased appreciably

and therefore, its subsequent respiratory rate did not rise much above that of the control. The following table (No. 6) brings out its contrast with the results

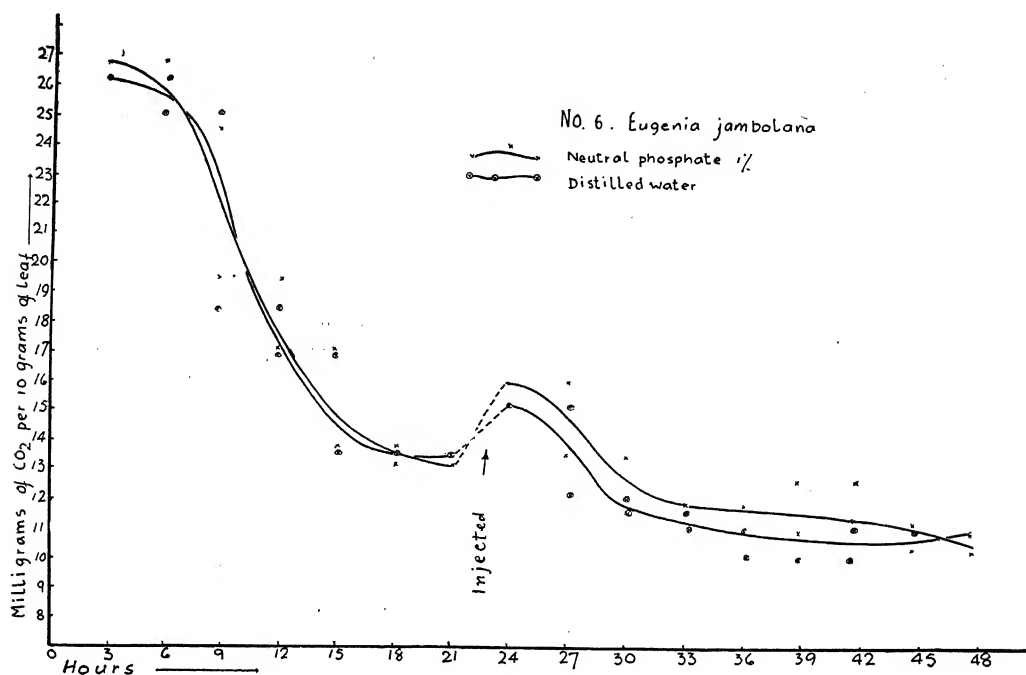


Fig. 6

given in Fig. 1, where the leaves were injected with phosphate from the very beginning.

Table 7

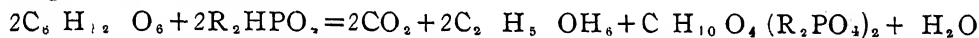
| Eugenia jambolana treatment of leaves. |                       | Mgs. CO <sub>2</sub> per 10 grams. of leaf. | Diff. between A and B. | Time.           |
|--|-----------------------|---|------------------------|-----------------|
| Results from Fig. 1                    | A. Phosphate only ... | 174.5                                       | 29.6 Mgs.              | First 24 hours. |
|  | B. Water only ...     | 144.9                                       |                        |                 |
| Results from Fig. 6                    | A. Phosphate only ... | 100.1                                       | 8.6 Mgs.               | Last 24 hours.  |
|  | B. Water only ...     | 91.5  |                        |                 |

It may be said that the diminution of the difference between the CO<sub>2</sub> values of the phosphate-injected and water-injected leaves is primarily due either to the depletion of phosphate in some way or somehow to its removal from the metabolic centre. The results just dealt with, (table 7) seem to go against such a suggestion, as injection of starved leaves with phosphate did not raise the OC<sub>2</sub>

output much above that of the water-injected ones. So that when sugar is less and phosphate is retained at the original value, the effect of the latter on respiration is almost negligible.

VI. *The phosphate sugar effect.*—The above considerations seem to indicate that phosphate by itself would not, very possibly, affect respiration in any marked degree, if respirable sugars are wanting, or are present in small quantities. Such a suggestion is supported by the fact that phosphate-sugar mixtures accelerate respiration very much more than either of them singly and that phosphates quicken respiratory rate more in the beginning, when the leaves are more sugary, than towards the end when sugar content is greatly diminished due to continuous starvation. Such a combined effect of sugar and phosphate seems to be possible only when the latter is mixed with anhexose sugar; with a disaccharide such an acceleration would probably be delayed till it is hydrolysed to monosaccharides.

VII. *The possible mechanism of phosphate reaction.*—The possible connection of phosphates with alcoholic fermentation has been brought out by the investigations of Harden and Young, as being the formation of hexose-phosphate and its consequent hydrolysis. Hence the addition of soluble phosphates to a fermenting liquid accelerates the rate of fermentation. It therefore seems probable that the acceleration of the rate of anaerobic  $\text{CO}_2$  output of leaves injected with phosphate is to be traced to the increased formation of hexose-phosphate according to the reaction:—



This view is all the more strengthened by the fact that acceleration of  $\text{CO}_2$  production is the greatest in the case of leaves injected with a mixture of phosphate and glucose.

Lyon while accepting the above view in the case of increased anaerobic production of  $\text{CO}_2$  by phosphate, is of opinion that in the aerobic phase, the acceleration of  $\text{CO}_2$  output is due to their "action as a promoter catalyst toward oxidases."

Against this there is the widely accepted theory that aerobic and anaerobic respirations have common initial stages and whether, after this, the ultimate respiratory material will break into water and  $\text{CO}_2$  or alcohol and  $\text{CO}_2$  is determined by the presence or absence of oxygen. The names of Kostychev and Palladin among many others is specially associated with such a theory. It implies that anything which affects the preliminary stages of anaerobiosis in one way will similarly affect the aerobic phase as well since both have a common beginning. Moreover, if phosphates act toward oxidases as promoter catalysts, all the available sugar, however small in quantity, ought to be oxidised at an accelerated rate, and consequently the  $\text{CO}_2$  output ought to be maintained at a higher level so long as oxidisable carbohydrates are available. But such a level of  $\text{CO}_2$  was not maintained in the experiments described above, for the final  $\text{CO}_2$  value was far lower than

what was initially. Moreover the various ratios obtained from aerobic  $\text{CO}_2$  values correspond with those obtained anaerobically and even with those obtained from the extra amount of  $\text{CO}_2$  output of the after-effects. This common ratio perhaps points out that the reactions responsible for the increased  $\text{CO}_2$  output of phosphate-injected leaves, may be the same both in aerobic and anaerobic forms of respiration. It may be however that Lyon's explanation is not totally exclusive of the possibilities of other reactions as well. Probably the acceleration of  $\text{CO}_2$  production should be traced to more causes than one. And the possibility of such an increase through a combination of simple sugars and phosphate at once commends itself.

#### SUMMARY

Experiments have been carried out on leaves *Eugenia jambolana* and *Allium tuberosum* to study the effects of phosphates on respiration both in aerobic and anaerobic conditions.

It has been found out the acceleration of  $\text{CO}_2$  output is the greatest when the leaves are injected with a mixture of phosphate and glucose; injection with phosphate alone causes more  $\text{CO}_2$  production than that with sugar alone; and both phosphate and sugar individually have a greater effect than injection with distilled water. This holds good both in the aerobic and anaerobic production of  $\text{CO}_2$ .

The acceleration is highest in the beginning of experiments and decreases with time.

Injection of starved leaves with phosphate causes very little change in  $\text{CO}_2$  output.

Sugar-estimations reveal the fact that phosphate-injected leaves utilize more sugar than non-phosphate ones.

It has been suggested that phosphates have very little effect on respiration when very little sugar is available for respiratory purposes.

The suggestion has been put forward that the phosphate acts through the intermediate stage of hexose-phosphate.

I must thank Prof. J. H. Mitter for the keen interest he has taken and Dr. S. Ranjan for help and guidance in preparing this paper.

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# ON AN ECHINOSTOME CERCARIA—CERCARIA PALUSTRIS—WITH NOTES ON ITS LIFE-HISTORY

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During the months of July to October in Allahabad one of the common Indian Snails—*Indio-planorbis exustus* (Deshayes)—is heavily infected with an Echinostome Cercaria—*Cercaria palustris* n. sp. The collar spines are very inconspicuous and often escape notice unless examined under an oil immersion lens. Faruqi (1930, 1205) has recently described—*Cercaria mehrai*—a cercaria completely spineless, but very similar in appearance to *C. palustris*, collected from the same host from Handia, a village about 25 miles east of Allahabad.

The author's personal examination of a large number of snails from Handia during the month of September has convinced him that *C. palustris*, so commonly found at Allahabad, is of common occurrence at Handia in that part of the year, and that unless a very high magnification is used, it is practically impossible to see the collar-spines which are present in it. The rate of infection was much higher than that of *C. mehrai* during the middle of September: out of 168 snails examined 103 were found infected. The rate, however, gradually decreased until in December and January when it was practically the same as that of *C. mehrai*. Faruqi has not mentioned any definite period when his observations were made and the writer is therefore unable to compare his rate of infection with the present rate. *C. palustris* presents certain striking similarities with *C. mehrai*, but at the same time it shows certain important features, which have either been overlooked by Faruqi in *C. mehrai*, or are entirely absent in it, as his description shows. I have examined a large number of snails from the same locality where Faruqi got his material from, but I have never come across a single specimen of *C. mehrai*. This fact confirms my suspicion that the latter species may be the same form as that described by me and that Faruqi may have failed to observe such important features as the collar spines and the intestinal caeca which are hardly visible under ordinary magnifications. But, in view of these important discrepancies in the description of *C. mehrai*, and my form, I do not think it proper to include my species under the same name and feel justified, under the circumstances, to create a new species for it, though, it is quite possible, as I have already pointed out, that further work may reveal the necessity of bringing both these species together as synonyms under one species.

The author wishes here to express his sincere thanks to Dr. H. R. Mehra for his help and guidance and to Prof. D. R. Bhattacharya for the provision of facilities for work in the department. Acknowledgments are also due to Prof. F. J. Meggitt for his suggestions and the use of his personal library.

### CERCARIA

The cercariae emerge from the body of the snail in hordes and wriggle actively in water in an undulating manner by movements of both the body and tail. While swimming the cercaria curves its body ventrally, occasionally sinking to the bottom and there crawling by alternately contracting and expanding its body and gripping tightly the surface of the object with the suckers. Due to extreme contraction and expansion the size varies considerably as shown by the following table:—

|         |                     | Contracted. | Expanded. |
|---------|---------------------|-------------|-----------|
| Body: { | Length ...          | 0' 231*     | 0' 456    |
|         | Maximum breadth ... | 0' 185      | 0' 072    |
| Tail: { | Length ...          | 0' 252      | 0' 483    |
|         | Maximum breadth ... | 0' 063      | 0' 045    |

The following measurements are of a semi-contracted specimen:—

|                              |     |     |                 |
|------------------------------|-----|-----|-----------------|
| Dimensions of ventral sucker | ... | ... | 0' 057 × 0' 05  |
| Dimensions of Oral sucker    | ... | ..  | 0' 045 × 0' 04  |
| Dimensions of Pharynx        | ... | ... | 0' 023 × 0' 019 |

Changes in size of the body also affect its general outline. At maximum expansion the two lateral margins are more or less parallel, pear-shaped in a semi-contracted stage, and more or less rounded in fully contracted condition. Inside the cuticle is a granular layer, probably representing the *epidermis*, apparently absent from the tail. Beneath the epidermis are numerous, more or less spherical, cystogenous cells of refractile appearance and filled with "rod-lets" arranged in parallel rows. These cells are more numerous in the periphery than in the centre and cover other organs of the body. Their number is much larger in older specimens, which, on account of their presence make the animal less transparent and more difficult to study. Both the body and the tail are provided with longitudinal and transverse muscles, which are specially well-developed and, therefore, more active in the region between the suckers than in any other part of the body, so that the great changes in the dimensions of the body due to the contraction and expansion of these muscles effect greatly the preacetabular region.

The tail, when extended, is a little longer than the body, but during semi-contracted condition of the cercaria it is shorter than the body length. It is attached on the ventral aspect of the body and except its terminal portion it is less contractile

\* All measurements are in millimetres,



than the body and is not easily detached even in specimens, that have had a free active existence of over eight hours. Beneath the cuticle of the tail lies a layer of strong circular muscle fibres, followed more internally by a layer of longitudinal fibres. More internally the tail is composed of parenchymatous tissue, through the centre of which runs the main excretory caudal canal. The terminal end of the tail is very contractile and the cuticle surrounding it very thin.

The ventral sucker is slightly shorter antero-posteriorly than in its transverse diameter and is situated nearly in the posterior one-third of the body. The oral sucker lies anteriorly close to the cutis and, like the ventral sucker, is shorter antero-posteriorly. On the surface of the body close to the posterior margin of the oral sucker are collar-spines, only visible under high magnifications. Owing to the minuteness of the spines, and also to the overcrowding of the cystogenous cells, it is difficult to count their exact number. The number was, however, found to be twenty-nine or a few less, as counted in a few specimens, while occasionally in the encysted stage as many as forty spines were observed to be present. They are arranged in two rows, one alternately above the other, in a dorsally incomplete circle.

The mouth is subterminal, leading into the cavity of the oral sucker and followed by a long prepharynx. The pharynx is muscular. The oesophagus is a little thicker and longer than the prepharynx and runs between two rows of gland cells lying in the centre of the body. Very close to the anterior margin of the acetabulum, it bifurcates into two long caeca, which curve first outwards, then inwards, to end blindly at the hinder end of the excretory bladder. The caeca are difficult to see except when filled with granular food particles or when there is a slight congestion of the cystogenous cells. The six salivary gland cells lie in two longitudinal rows, one on each side of the oesophagus. Each cell is provided with lobed margins, a well-developed nucleus in the centre, and granular protoplasm around the periphery. The ducts are very inconspicuous and could not be observed. Near the anterior margin of the oral sucker on the both sides of the median line, certain tubules were, however, seen, which I presume are continuations of the salivary ducts. Faruqui (1930) has failed to observe any salivary gland cell in *O. mehrai*, but on the other hand finds a mass of hexagonal cells, varying in number from six to eight, very similar in position to the salivary gland cells of *O. palustris*, and which he considers as cells of the vagina.

The excretory bladder is thick-walled and situated at the extreme hinder end of the body. Its shape differs according to the extent of contraction and expansion: during contraction it assumes more or less a spherical appearance. The primary excretory tubes are thinwalled and narrow. They arise from the anterior aspect of the bladder through a common orifice and take a wavy course outwards and forwards. At the level of the anterior part of the acetabulum, the tube widens to accommodate a series of large six or seven spherical or oval excretory granules of

the usual refractile appearance. This dilated part of the main duct occupies laterally a great part of the body length and becomes constricted into a narrow tube at about the region of the pharynx, when it bends upwards and downwards in the form of a loop, running dorsally in close apposition to the dilated part as far as the level of the acetabulum. From there it is deflected laterally and continues back to the posterior end of the body. At the side of the bladder the tube turns forwards to traverse for the third time the entire length of the body (Fig. 2). In the body twelve pairs of flame cells could be seen, but it is possible that the number may be larger. Of these five pairs are pre-acetabular, one at the level of the acetabulum and the remaining six pairs post-acetabular in position. The first pair lies close against the posterior margin of the oral sucker, the second and the third laterally in the body, one anterior and the other posterior to the excretory loop; the fourth near the third excretory granule; the fifth close to the anterior margin of the acetabulum; the sixth at level with the acetabulum; the seventh posterior to the acetabulum, and the remaining five pairs near and outside the bladder. The flame cells are absent from the tail, in which the excretory system is represented only by a median duct arising from the posterior margin of the excretory vesicle and opening to the exterior to the left side close in front of the abrupt ending of the tail. The genital organs are represented by a mass of small rounded cells in the post-acetabular region, which on account of their size appear to be cells of the ovary: in some cercariæ they develop into a compact mass of larger cells with prominent nuclei and granular cytoplasm. Some cercariæ of the same species obtained from Rangoon showed in addition a few groups of spherical cells near the anterior margin of the ventral sucker.

#### REDIA

Development of the cercariæ takes place in rediæ. These are found closely packed in the liver mass of the host from which they are easily detached. They generally occur in large numbers, sometimes exceeding two hundred fifty in number. Freshly detached rediæ are orange-brown in colour, due to the presence of particles of the liver in which they lie embedded. Rediæ obtained from a single host are of various stages and sizes having guts in different proportions to the body length. A well-developed redia measures approximately 2.66 in length whereas a young one measures only 0.457. The mouth is terminal followed by a well-developed protrusible pharynx, measuring  $0.042 \times 0.036$ . The pharynx is followed by a deep brown rhabdocœle gut, the colour being imparted by the food particles. A little distance behind the pharynx lies the collar, a band-like thickening around the body, slightly projecting from it. The collar is inconspicuous in most of the rediæ but it is well-developed in the young forms. Posterior to the collar lies a depression in the body wall, in the centre of which there is a crescentic orifice, the 'birth-pore'. In the hinder part of the body the redia is provided with

a pair of locomotor processes with which it slowly moves on. Cercariæ are densely packed in the body cavity of a mature redia and emerge out of the birth-pore by either their anterior or posterior ends.

#### METACERCARIA.

The cysts of *C. palustris* were commonly found in the tissues of *Indo-planorbis exustus* (Deshayes) but occasionally such cysts were also obtained from *Limnea acuminata*. The number of cysts varies in different snails, ranging from approximately a dozen to nearly four hundred. The author's personal observations have led him to believe that the cercariæ emerge from the tissues of their hosts and re-enter fresh snails to encyst, failing which they die and sink. This is in opposition to the belief held by Johnson (1920), who holds that this procedure necessitates a waste of individuals without any apparent benefit.

A well-developed cyst measures as follows:—

|                   |   |                |       |
|-------------------|---|----------------|-------|
| Cyst:             | { | Length ... ..  | 0'153 |
|                   |   | Breadth ... .. | 0'126 |
| Oral sucker:      | { | Length ... ..  | 0'028 |
|                   |   | Breadth ... .. | 0'04  |
| Ventral sucker:   | { | Length ... ..  | 0'03  |
|                   |   | Breadth ... .. | 0'045 |
| Oesophagus:       |   | Length ... ..  | 0'03  |
| Intestinal caeca: |   | Breadth ... .. | 0'01  |

The cyst is covered by a chitinous wall, the thickness of which differs in different cases, the minimum thickness being 0'004 and the maximum 0'007. The inconspicuous collar spines of the cercariæ are very prominent in the cyst. Their correct number is very difficult to determine but on the average it appears to be twenty-nine. In a few cases as many as forty spines have been noticed. It is possible that all the collar spines may not be visible due to retraction of this part of the body in the living cyst and this probably accounts for the great variation in number of collar spines in different cysts. The cyst is transparent and refractile. It can be separated from its wall by exerting a slight pressure over it under a cover-slip. The mouth in the encysted cercaria is terminal opening into the cavity of the oral sucker, followed by a prepharynx. The pharynx is muscular and followed by a well-developed intestine, which bifurcates in front of the acetabulum to continue into two caeca ending blindly near the hinder end of the excretory bladder. The gut is quite prominent and is filled with food granules in its entire course. The excretory system in the cyst is very similar to that of the cercariæ, but the excretory loop is filled with a number of excretory granules.

## DISCUSSION

*Cercaria palustris* closely resembles *Cercaria mehrai* but for three distinctive features, i.e., the presence of somewhat inconspicuous collar spines, bifurcation of the œsophagus into two narrow caeca, and the presence of gland cells. It appears, therefore, necessary to treat it as a new species. The resemblance between the two species is marked in the structure of the tail, suckers and the gut (excluding the caeca which are reported to be absent in *O. mehrai*). The cystogenous cells are also similar though more or less spherical instead of 'rectangular' or 'irregular geometrical shape' as in the latter species. The shape of the excretory bladder and the course of the excretory ducts are almost similar with only minor differences. The flame cells also correspond more or less in number and position, there being twelve pairs in the present species and ten in *O. mehrai*. Owing to the highly contractile nature of the cercariæ no special importance can be attached to the difference in size of the body and tail.

According to the existing system of classification of the Echinostome Cercariæ it is extremely difficult to assign this cercaria to any particular group. It resembles and differs all the groups in great features except the 'Megalura' created by Cort (1915) from which it can be sharply separated on account of profound differences. The characters, which *O. palustris* has in common with the 'Echinotoides,' 'Coronata' and 'Echinata' groups are given in tables 1, 3, and 5 respectively, while the differences between them are given in tables 2, 4, and 6.

Table 1.—Resemblances with the 'Echinotoides' group.

- (a) Collar spines arranged in double rows.
- (b) Cystogenous cells with parallel rods of protoplasm.
- (c) Extreme tip of the tail pointed to a conical process and capable of independent contraction and expansion.
- (d) Thin cuticle surrounding the terminal end of the tail.
- (e) Alimentary system complete with distinct lumen.
- (f) A few salivary gland cells with granular protoplasm.

Table 2.—Differences with the 'Echinotoides' group.

- (a) Absence of fin-fold in the tail.
- (b) Ventral sucker longer in transverse diameter.
- (c) The course of the excretory tubes different.

Table 3.—Features of resemblance with the 'Coronata' group.

- (a) Double rows of spines in the collar of approximately equal size.
- (b) Cystogenous cells with parallel rods of protoplasm.
- (c) No fin-fold on the tail.

Table 4.—Differences with the 'Coronata' group.

- (a) Difference in the course of the excretory tubes.
- (b) Variation in the proportionate length of the gut of rediæ with body length.

Table 5.—Resemblances with the 'Echinata' group.

- (a) Double rows of spines in the collar.
- (b) No fin-fold on the tail.
- (c) Course of the excretory tubes identical.
- (d) Variation in the length of gut in different rediæ
- (e) Encystment of the cercariæ within the tissues of mollusc host.

Table 6.—Differences with the 'Echinata' group.

- (a) Absence of spines on the body.
- (b) Cystogenous cells not with granular contents.
- (c) Salivary glands not composed of numerous small pyriform cells.

From the foregoing comparison it may be seen that the existing classification of Echinostome cercariæ is unsatisfactory. *Cercaria palustris* appears to be a transitional form between the various groups. If, as is held by Cort, Faust, Sewell and others, the excretory system be considered the sole, or the chief character of systematic importance, then *Cercaria palustris* should be placed in the 'Echinata' group. This, however, involves a complete unimportance of all other characters, which is liable to result in an unnatural system of classification.

## EXPLANATION OF PLATES.

- Fig. 1. *Cercaria palustris* n. sp.—ventral aspect (Semi-diagrammatic).
- Fig. 2. *Cercaria palustris* n. sp.—showing the excretory system (diagrammatic).
- Fig. 3. Redia of *Cercaria palustris* n. sp.—ventral aspect (camera lucida drawing).
- Fig. 4. Cyst of *Cercaria palustris* n. sp.—ventral aspect (camera lucida drawing).
- Fig. 5. Cysts of *Cercaria palustris* n. sp.—(microphotograph: under low power).
- Fig. 6. Cyst of *Cercaria palustris* n. sp.—(microphotograph, under oil immersion lens).

## LETTERING TO FIGS. 1—6.

C. cyst, cer. cercaria, cet. caudal excretory tube, cr. collar region, cs. collar spines, e.g. excretory granule, ep. excretory pore, es. oesophagus, ev. excretory vesicle, fc. flame cell, glc. cystogenous cell, ie. intestinal cæcum, lp. locomotory process, met. mainlateral excretory tube, os. oral sucker, ph. pharynx, pph. prepharynx, rd. rhabdocœle gut, sg. salivary gland cell, vs. ventral sucker or acetabulum.

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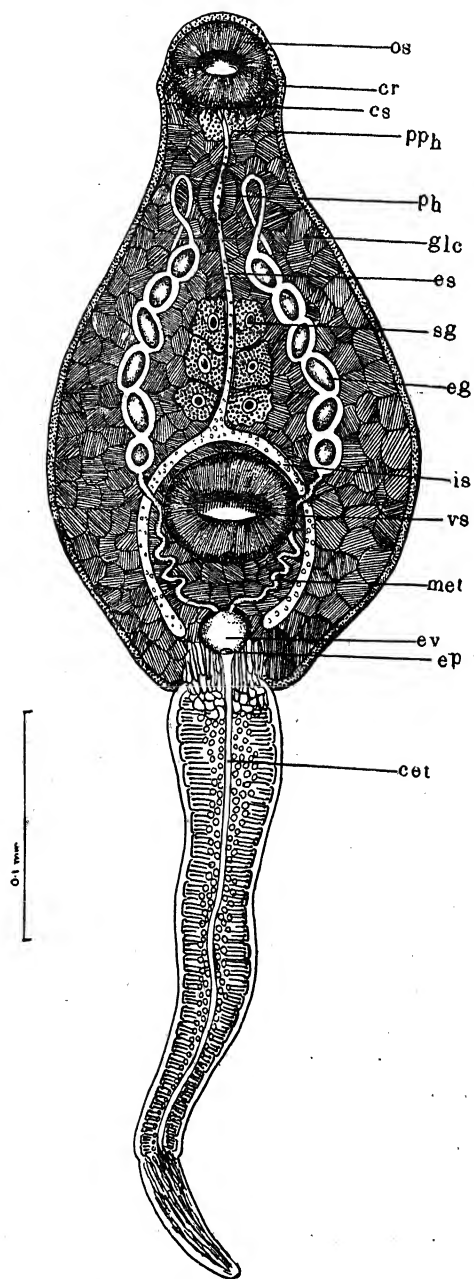


Fig. 1.—*Cercaria palustris* n. sp.—Ventral aspect.

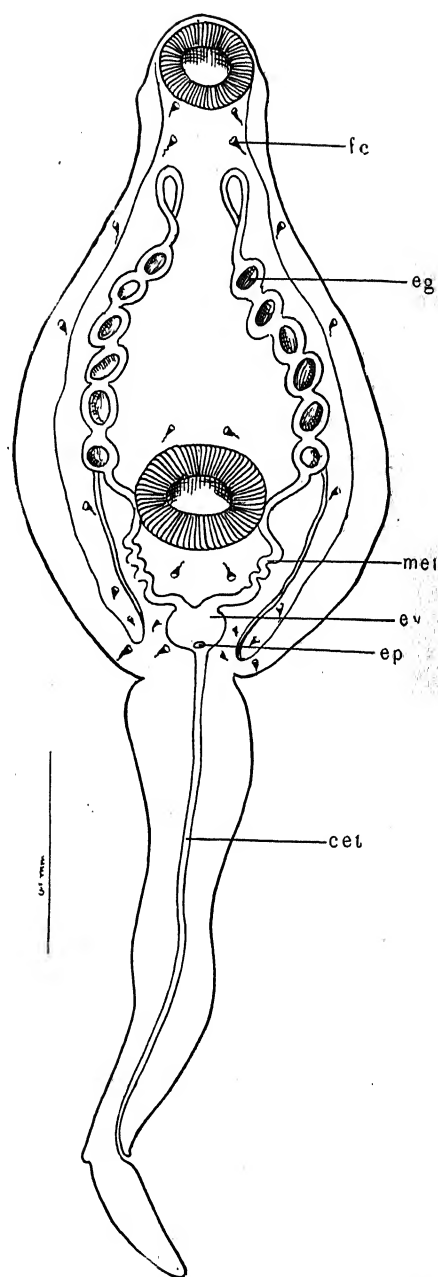


Fig. 2.—*Cercaria palustris* n. sp.—showing the excretory system.

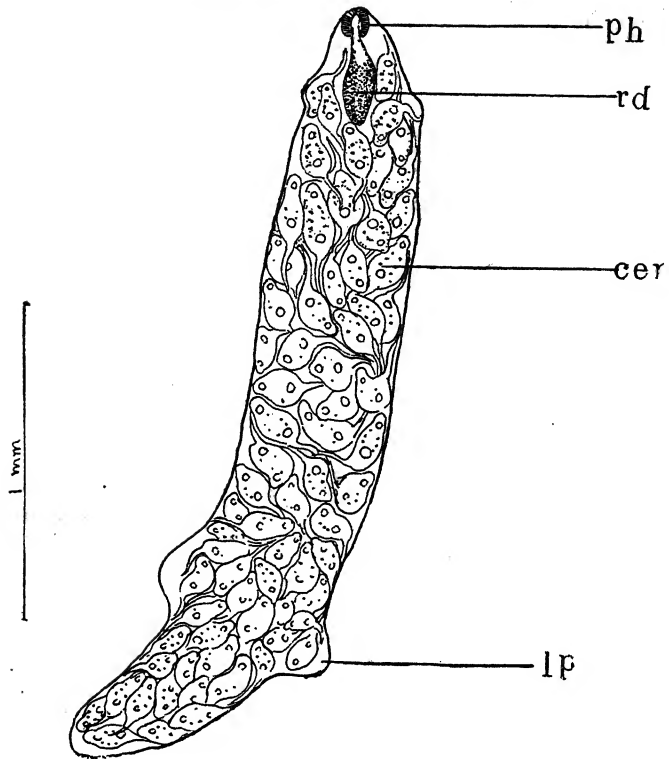


Fig. 3.—Redia of *Cercaria palustris* n. sp.

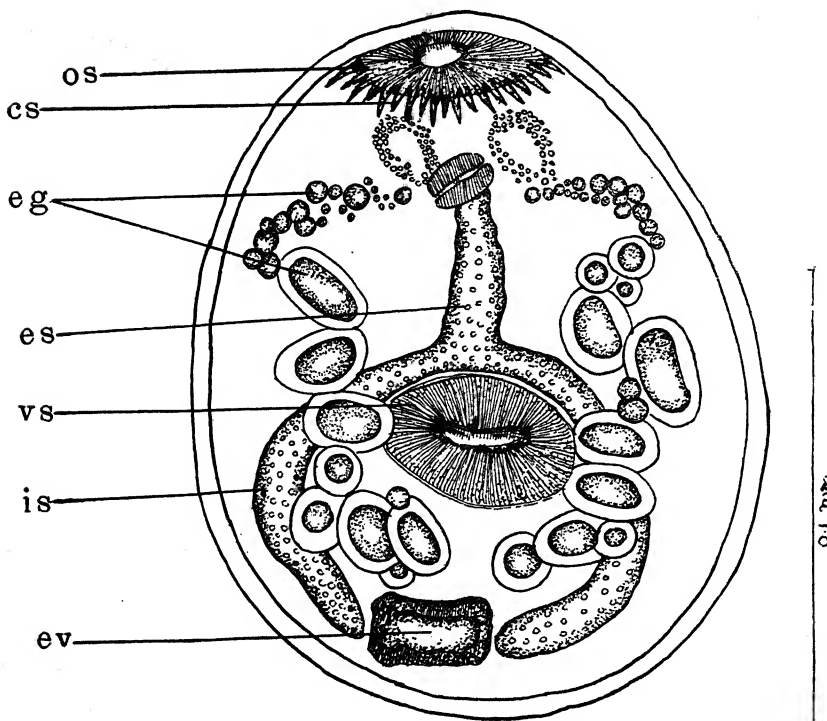


Fig. 4.—Cyst of *Cercaria palustris* n. sp.—Ventral aspect.

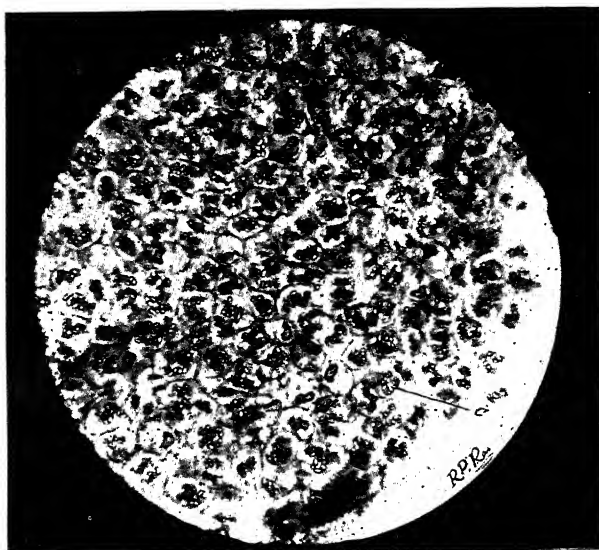


Fig. 5.—Cysts of *Cercaria palustris* n. sp.

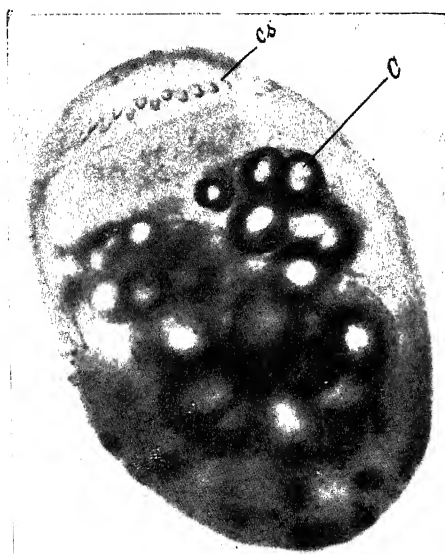


Fig. 6.—Cyst of *Cercaria palustris* n. sp.



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NEW BLOOD FLUKES OF THE FAMILY SPIRORCHIDÆ STUNKARD  
FROM INDIAN FRESH-WATER TORTOISES WITH DISCUSSION  
ON THE SYSTEMATIC POSITION OF THE GENUS  
*COEURITREMA* N. G. AND THE RELATIONSHIPS OF  
THE FAMILIES OF BLOOD FLUKES.—PART I.

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**Introduction**

THE blood flukes of birds and mammals constituting the family Schistosomatidæ Looss, 1899 syn. Bilharziidæ Odhner, 1912, of turtles belonging to the family Spirorchidæ Stunkard, 1921 syn. Proparorchidæ Ward, 1921, and of fishes included in the families Aporocotylidæ Odhner, 1912, and Sanguinicolidæ Graff (1907) have received much attention during the last several years, and it is well known that they form a well-defined group of closely-related forms—the Superfamily Schistosomatoidea Stiles and Hassal, 1926. Poche (1925) has, however, classified the blood flukes into two superfamilies, the Sanguinicolida containing the Spirorchidæ, Aporocotylidæ and Sanguinicolidæ and the Schistosomatida containing the family Schistosomatidæ. While I do not intend to discuss in this paper the usefulness or propriety of the two superfamilies created by Poche it is worth while to mention that ever since the publication of the memorable paper by Odhner in 1912 about the relationships of *Liolope*, *Hapalotrema*, *Bilharziella*, *Ornithobilharzia* and *Bilharzia*, the idea of the close affinities of the families of blood flukes has been gaining ground, and now it is established beyond doubt that the families Schistosomatidæ, Spirorchidæ, Aporocotylidæ and Sanguinicolidæ are closely related forming a well-defined group, and that there will not be much purpose served for a scheme of natural classification if we create two superfamilies for them. Travassos (1928) also prefers to combine the two superfamilies Sanguinicolida and Schistosomatida in one superfamily under the name of Schistosomatoidea Stiles and Hassal, 1926.

In the following pages I have described two new species of a new genus *Coeuritrema* belonging to the family Spirorchidæ, which, as will be seen from

the discussion at the end of the paper is closely related to the genera *Hapalotrema*, *Hapalorhynchus* and *Vasotrema*, and shows certain remarkable features in its anatomy, which throw much light on the origin of the Schistosomatidæ confirming the view put forward by Odhner about the close affinities of these blood flukes with the subfamily Liolopinæ of the family Harmostomidæ Odhner, 1912. It is interesting to note that this genus stands nearer *Liolope*, the type genus of the Liolopinæ than *Hapalotrema* in the general topography of its organs, presence of two testes with the ovary between them in the posterior half of the body and position of the genital opening about the middle of body length to the left side behind the ventral sucker. It appears, therefore, clear that the superfamily Fascioloidea stands connected with the superfamily Schistosomatoidea through the Harmostomidae Odhner, which is closely related to the Clinostomidæ Lühe.

### ***Coeuritrema lyssimus* Nov. Gen., Nov. Spec.**

The trematodes of this species were collected by me in 1931 and 1932 from the ventricle of the heart of soft-shelled turtles *Lysemys punctata* at Allahabad. In all I examined sixteen turtles, out of which nine were found infected with these parasites. The rate of infection, therefore, seems to be nearly fifty per cent. The number of parasites found in a single host is generally large, more than a dozen. Three hosts were, however, found infected with 5–10 specimens each. In one case only three specimens were obtained. The distomes are more or less firmly attached to the walls of the ventricle and do not come out at once when the ventricle is opened. Some take a few minutes to come out, others a longer time; some took 20 minutes to half-an-hour to come out in the normal salt solution in which the ventricle cut into two halves was kept. When freed in salt solution they do not show any active movements; sometimes they bring their anterior and posterior ends close together and become bent in the form of a loop. They also contract slightly on the application of fixing fluids.

The body is thin and very transparent, and in preserved specimens it is generally hollowed out in the form of a shallow groove. It is somewhat conical in shape, broad and somewhat rounded near the posterior end and narrow in front of the ventral sucker ending to a blunt point at the anterior end. The size is small, 1.53–1.92 mm. in length and 0.46–0.48 mm. in greatest breadth, which lies in the region of the ovary. In the region of the intestinal bifurcation the breadth measures 0.27–0.28 mm., and in that of the ventral sucker 0.23–0.3 mm., behind which it gradually increases, measuring 0.36 mm. in the region of the genital opening and 0.46 mm. in the region of the anterior testis and the ovary, where it reaches the maximum limit. Immediately behind the ovary it slightly diminishes, measuring 0.43 mm. in the region of the posterior testis. In the region of the excretory bladder or the ends of intestinal cæca it measures 0.288 mm. One specimen measured

1.37 mm. in length and 0.35 mm. in maximum breadth. All the above measurements are taken from entire mounts. The hinder end is usually spatulate and flattened depending upon the state of contraction and notched in the centre, where the excretory bladder opens. Some specimens when much contracted show a curiously broad shape of the body with a more or less uniform breadth from behind the ventral sucker to the hinder end. Specimens of smaller size, as a rule, become easily contracted to assume such curious shapes. The body-wall is covered with small conical papillæ or tubercles, which extend from a little distance behind the oral sucker to the hinder end, measuring 0.012 mm. in length and 0.18 mm. in maximum breadth at the base. They are sparse in front of the intestinal bifurcation, but behind the acetabulum they are numerous and more closely situated. Their free ends are somewhat rounded or bluntly pointed and directed straight outwards or upwards, but not backwards like the usual chitinous spines. The small rod-shaped spines characteristic of the blood flukes are present only in the region of the genital pore and cirrus sac. There are hardly any muscle fibres visible in the body-wall, and there is no muscular layer present outside the epithelium lining the intestinal cæca.

The oral sucker is terminal and partly projects out from the anterior end above the general surface of the body, but ordinarily it is not so much protrusible as in the genus *Spirorchis*. It has a circular outline, measuring 0.1–0.12 mm. in diameter; occasionally it is a little longer than broad. The ventral sucker is much larger and stouter, measuring 0.17–0.19 mm. in diameter and 0.14–0.15 mm., in depth, *i.e.*, a little less than twice the size of the oral sucker. In two specimens however, the ventral sucker measured 0.14–0.15 mm. in diameter and the oral sucker 0.112 mm. in length and 0.096 mm. in breadth. The ventral sucker lies close behind the intestinal bifurcation at about one-third body-length from the anterior end, occupying nearly the entire depth and a great portion of the breadth of the body, and has the form of a deep cup with a short base capable of entire protrusion from the general body surface. It is muscular, having a well-developed layer of radial muscles with an outer layer of longitudinal muscle fibres; the thickness of its wall is about double of that of the oral sucker. The pharynx is absent. The oesophagus is straight and more or less of uniform breadth, measuring 0.195–0.256 mm. in length and 0.045–0.075 mm. in breadth (in one specimen 0.33 mm. long). It is closely surrounded by salivary gland cells, which are found in large numbers forming a bulbous mass before it passes into the intestinal bifurcation; the gland cells are also found in large numbers around its anterior part. The intestinal cæca turn backwards soon after their origin and extend to a little distance in front of the hinder end. They are pressed closely against, or slightly overlapped by the ventral sucker, behind which they converge inwards towards each other mesially, the left curving more deeply than the right, but soon turn outwards to occupy a lateral position. Behind the posterior testis they again undulate twice or thrice but less markedly than before. The

cæca undulate so characteristically behind the ventral sucker and the posterior testis that they enclose between them an intracæcal zone, in which the gonads with their associated ducts, vesicula seminalis and cirrus sac lie, and this I propose to call the genital field. The cæca are very narrow around and a little behind the ventral sucker. The genital opening lies dorsally to the left side of the body outside the left intestinal cæcum, half-way between the median line and the left body margin, in the region enclosed by the first characteristic loop of the left cæcum, a little distance, *i.e.*, 0.12 mm. behind the ventral sucker and a little in front of the middle of body. In a contracted specimen the intestinal cæca come so near each other behind the ventral sucker and the posterior testis that they practically meet enclosing the genital field on all sides between them, reminding one of the posterior union of the intestinal cæca in the family Schistosomatidæ. In the region of the genital pore the left cæcum comes to the right side of the median line lying close to the right cæcum (Fig 5). As seen in a transverse section passing through the genital pore the dorsal side of the body in this region is flattened and the ventral side arched.

The testes, two in number, lie in the posterior half of the body in the genital field with the ovary between them (Figs. 1 and 2). The anterior testis lies to the right side pressed against the right intestinal cæcum and close behind the cirrus sac, 0.288 mm. behind the ventral sucker, 1.04 mm. behind the anterior end and 0.62 mm. in front of the hinder end. It is roughly triangular or somewhat heart-shaped with a broad flat or slightly concave anterior margin and narrow rounded or somewhat bluntly pointed posterior end, and measures 0.14–0.16 mm. in length, 0.14–0.176 mm. in greatest breadth and 0.144 mm. in depth, occupying the entire depth of the body and touching the dorsal and ventral body walls. In one specimen it measured 0.096 mm. long and 0.1 mm. broad. The ovary lies between the two testes, immediately behind the anterior testis and in front of the posterior testis to the left side of the median line with its outer wall pressed closely inside the left intestinal cæcum. It is not much lobed but has a triangular or somewhat oval form with an inwardly directed process or lobe from which the oviduct arises, measuring 0.12–0.18 mm. in length, 0.05–0.1 mm. in greatest breadth and 0.051–0.11 mm. in depth; the lobe arises from its mesial surface, a little behind or about the middle of its length. The ovary appears as a compact mass of ova of large size of 0.024–0.027 mm. diameter and easily visible under the low power of a microscope. The oviduct lies in the median line and is lined with an epithelium of cubical cells with prominent nuclei. The receptaculum seminis, 0.09 mm in length and 0.033 mm in greatest breadth, is a somewhat spherical or pear-shaped sac filled with sperms, which lies to the right side immediately in front of the posterior testis, close inside the right intestinal cæcum, in the same line with the anterior testis and just behind the level of the posterior margin of the ovary. The Laurer's canal arises from the inner side of the receptaculum seminis, near the point where the latter joins the oviduct and opens to the exterior

dorsally, slightly to the left of the median line, a little in front of the posterior margin of the ovary where it is lined with a thin layer of cuticle. The transverse vitelline ducts lie between the ovary and posterior testis in front of the receptaculum seminis, near the ventral body-wall. The vitelline reservoir lies in front of the transverse ducts in the median line or slightly to the right side and opens into the oviduct before the receptaculum seminis joins it. Both the vitelline reservoir and transverse ducts are composed of a solid mass of fairly large vitelline cells containing a prominent nucleus and vitelline granules. The oviduct after its junction with the receptaculum seminis passes into a small thin walled uterus, situated between the ovary and the anterior testis. The uterus is small and indistinguishable from the metraterm except by the absence of musculature in its walls. The metraterm is well developed and strongly muscular, measuring 0.27–0.32 mm. in length; it commences between the ovary and the anterior testis, in front of which it runs parallel to the cirrus sac, crossing the left intestinal cæcum to open to the exterior at the dorsally situated genital opening. It has greatest breadth, 0.03–0.08 mm. in its proximal part, *i.e.*, in the region between the ovary and anterior testis, where the ovum is usually found, while near the genital opening it measures 0.018–0.021 mm. in diameter. It is much more thick-walled in its distal part which lies to the left with the terminal part of the cirrus sac near the median line and the left and right intestinal cæca to the right side (Fig. 5). The posterior testis lies close behind the ovary and receptaculum seminis in the median plane of the body, 0.384 mm. distance in front of the hinder end. It is somewhat lobed, ovoid or rounded in shape, broad in front, and narrow behind, measuring 0.12–0.176 mm. in length, 0.084–0.16 mm. in greatest breadth and 0.075–0.12 mm. in depth, occupying the entire depth of the body and entire space between the laterally situated cæca; immediately behind it the cæca converge inwards coming near each other and joining in contracted specimens so as to mark the hinder limit of the genital field. The genital field, 0.4 mm. in length, occupies the third quarter of the body length.

The cirrus sac is large and thick-walled composed of circular muscle fibres, and is situated obliquely in the median line, in the anterior part of the genital field, with its base in close contact with and pressing the anterior face of the anterior testis near the right intestinal cæcum, and its terminal part near and outside the left intestinal cæcum on its way to the genital opening. It has a characteristic retort-shaped or flask-shaped appearance with a slight concavity anteriorly to the right side, in which lies closely pressed against it the vesicula seminalis. It measures 0.15–0.24 mm. in length, 0.045–0.084 mm. in greatest breadth a little in front of the basal end and 0.06 mm. in depth; in front of the middle of its length it measures 0.048–0.06 mm. in breadth. The vesicula seminalis is nearly spherical, pear-shaped or oval in outline, situated outside the cirrus sac and pressed closely against it in the concavity in its right wall, between it and the right intestinal cæcum, in level with and immediately behind the genital pore

It has thin parenchymatous walls and is filled with sperms, measuring 0.048—0.057 mm. in length, 0.024—0.042 mm. in greatest breadth and 0.045 mm. in depth; it becomes narrower near its hinder end, where it enters the cirrus sac. The pars prostatica lies within the cirrus sac as a narrow tube surrounded by a vacuolated mass of prostate gland cells. The cirrus is well developed and easily protrusible. When protruded it is seen to be continuous with, though somewhat constricted off from, the terminal portion of the cirrus sac, which lies within the genital atrium. It is an elongated cylindrical organ, swollen at the free terminal end and narrow at the base, lying flat on the dorsal surface of the body near the left body margin, and measuring 0.09—0.1 mm. in length, 0.075—0.09 mm. in greatest breadth at the end and 0.033 mm. in breadth at the base (Fig. 5). The cirrus sac opens to the right and the metraterm to the left side in the small genital atrium.

The vitellaria commence behind the acetabulum and terminate near the hind end just behind the blind ends of the intestinal cæca. They lie mainly outside the intestinal cæca covering them dorsally and ventrally, but immediately behind the acetabulum and the posterior testis, i.e., in the region of the cæcal loops they extend inwards uniting mesially, leaving, however, entirely uncovered the genital field and the excretory bladder. The follicles are large in size and closely crowded together. The transverse ducts arise between the ovary and the posterior testis and unite to form in front the vitelline reservoir, which lies ventrally to the oviduct. Only one ovum is contained at a time in the uterus or in the proximal part of the metraterm. The ovum is large, somewhat oval in shape, and produced into a narrow filament at each end, measuring 0.168 mm. in length with filaments, 0.096 mm. without filaments and 0.027—0.03 mm. in greatest breadth. In one specimen the ovum had one end produced into a small bluntly pointed filament and the other end indistinctly curled; in this case the entire ovum measured 0.096 mm. in length.

The excretory bladder is short but prominent, situated at the posterior end of the body in the median plane, behind and a little in front of the blind ends of the intestinal cæca. It consists of a short median stem, which bifurcates anteriorly at about the level of or a little in front of the blind ends of the cæca, into two short cornua or lobes lying near and parallel to each other. The main stem also gives off laterally two lobes behind each other on each side near the bifurcation. The tubular bladder and its diverticula are lined by a layer of columnar epithelial cells with no muscular layer outside. The excretory opening is terminal, situated in the middle of the notch at the posterior end of the body.

Habitat: Ventricle of heart.

Host: *Lissemys punctata* syn. *Emyda granosa*. Locality: Allahabad, India.

### ***Coeuritrema Odhnerensis* Nov. Spec.**

One specimen of this blood fluke was obtained from the ventricle of the heart of *Lissemys punctata* at Allahabad in October 1931. The body is thin, delicate

and very transparent, measuring 1.5 mm. in length, 0.224 mm. in maximum breadth in the genital field, *i.e.*, from the genital opening to the hinder limit of the posterior testis, 0.176 mm. in breadth in the region of the ventral sucker and 0.16 mm. in that of the intestinal bifurcation. It is narrow and elongated with bluntly-pointed ends, measuring 0.09 mm. in breadth at the anterior end and 0.06 mm. at the posterior end; just behind the oral sucker it slightly broadens attaining a breadth of 0.1 mm. The posterior end is not broad and notched in the middle as in *Coeuritrema lyssimus*, from which this species differs markedly in the shape of its body (Fig. 7). The body-wall is entirely free from tubercles or papillæ, which are well developed in the other species.

The oral sucker is larger than the ventral sucker, measuring 0.087 mm. in length and 0.075 mm. in breadth. It lies terminally at the anterior end and is much protrusible. The ventral sucker is delicate, much smaller and thinner with poorly developed musculature than that of *C. lyssimus*, measuring 0.06 mm. in length and 0.072 mm. in breadth, and lies a little in front of the hinder limit of the first third body length. The pharynx is absent. The œsophagus measures 0.27 mm. in length and 0.08 mm. in maximum breadth, and is surrounded by salivary gland cells, which lie in much larger numbers around the intestinal bifurcation. The intestinal cæca run backwards as soon as they arise, surrounding closely the ventral sucker and terminate a little distance in front of the hind end, just in front of the bifurcation of the short main stem of the excretory bladder. Behind the ventral sucker, at a distance of 0.075 mm. from it, they bend inwards towards the median line, the left more markedly than the right, to form the characteristic loops, which lie near each other separated by a narrow median region of 0.015 mm. diameter. Behind the genital field, *i.e.*, the posterior margin of the posterior testis they do not undulate to form loops as in the other species, but they run straight near and parallel to each other, ending 0.15 mm. distance in front of the hind end.

The excretory opening lies at the hind end of the body. The excretory bladder is narrow and tubular, situated at the hind end just behind the blind ends of the intestinal cæca; the main stem of 0.1 mm. length is a little longer than that of the other species and bifurcates into two short cornua, close behind the blind ends of the cæca. One small rather inconspicuous lateral lobe is given off on each side from the main stem just behind the point of bifurcation.

The genital opening lies dorsally to the left side in the region enclosed by the loop of the left intestinal cæcum, close outside the latter, 0.99–0.1 mm. distance behind the ventral sucker and a little in front of the middle of the body; it lies a little more forward than in *C. lyssimus*. The testes, two in number, lie in the posterior half of the body with the ovary between them in the genital field and are distinctly lobed. The anterior testis lies immediately behind the cirrus sac, 0.12 mm. distance behind the genital opening, somewhat in the median line, more to the right than the left side near the right intestinal cæcum by the intervening metraterm. It is irregularly lobed and rounded, measuring 0.105 mm. in diameter. The ovary

lies between the testes and has a characteristic flask-shaped outline with the neck part directed mesially and the main body part of an oval shape, 0.081 mm. long and 0.03 mm. broad, situated to the left side with its outer margin in close contact with the left intestinal caecum and its longitudinal axis parallel to the length of the body. The narrow mesially directed part 0.039 mm. long and 0.027 mm. broad, arises from the middle of its length and is continued into the oviduct. The receptaculum seminis filled with sperms lies to the right side close inside the right intestinal caecum with its narrow anterior part curved mesially, opposite to the ovary immediately in front of the posterior testis, and measures 0.054 mm. in length and 0.036 mm. in greatest breadth near its basal end. The transverse vitelline ducts and the vitelline reservoir lie as in the other species close behind the ovary, between it and the posterior testis. The posterior testis lies median, 0.454 mm. in front of the hinder end and immediately behind the ovary and the receptaculum seminis; it is lobed like the anterior testis with nearly equal long and broad diameters, measuring 0.096 mm. in length and 0.102 mm. in greatest breadth, and occupies the entire space between the two caeca. The gonads occupy nearly third quarter of the body length.

The cirrus sac is well developed with stout muscular walls, situated close in front of and pressing behind the anterior testis; it is crescent-shaped with a deep concavity in its right wall, which lies median with the vesicula seminalis opposite to it near the right intestinal caecum. It is approximately 0.18 mm. long and 0.054 mm. broad in its greatest diameter in the region a little in front of the concavity. It consists of a small basal part of 0.075 mm. length lying transversely and large vertical part lying adjacent to the left intestinal caecum. The vesicula seminalis of an oval shape lies to the right side touching the right intestinal caecum opposite to the middle part of the cirrus sac, and measures 0.054 mm. in length and 0.036 mm. in greatest breadth. The cirrus is well developed and protrusible. When protruded it shows a chitinous rugose surface without spines or hooks and has a characteristic stick-shaped form with a stumpy curved handle like terminal portion of 0.033 mm. length and 0.027 mm. breadth; the main part measures 0.045 mm. in length and 0.018—0.02 mm. in breadth.

The uterus lies between the mesial neck part of the ovary and the posterior margin of the anterior testis; it is not distinguishable from the metraterm, into which it soon passes. The metraterm is well developed with thick muscular walls, situated to the left side in close contact with the left intestinal caecum, between it on one side and the cirrus sac and the anterior testis on the other, measuring 0.25 mm. in length and 0.03 mm. in breadth. Near its terminal end it crosses ventrally the left intestinal caecum to open into the shallow genital atrium. Only one ovum is contained in the uterus or the proximal part of the metraterm, which in consequence is much dilated. The ovum is oval in shape and produced into a coiled filament at one end and indistinctly seen elongated filament at the other, measuring 0.09 mm. in length without filaments and 0.03 mm. in greatest breadth.



The vitellaria are extensive, situated laterally overlapping the intestinal cæca and uniting mesially behind the ventral sucker, in the region between it and the genital pore, and in the intracæcal region behind the posterior testis to the blind ends of the cæca, leaving entirely free the genital field. They commence at the intestinal bifurcation and terminate a little behind the blind ends of the cæca at about the bifurcation of the short stem of the excretory bladder.

Habitat: Ventricle of heart.

Host: *Lissemys punctata* syn. *Emyda granosa*.

Locality: Allahabad, India.

### Remarks on the Species of the Genus *Coeuritrema*

It will be apparent from the foregoing description that *Coeuritrema odhnerensis* and *Coeuritrema lyssimus* resemble each other closely in the anatomy and topography of organs and therefore must be referred to the same genus. Both the species are characterised by the presence of two suckers, a long œsophagus surrounded by gland cells, intestinal bifurcation close in front of ventral sucker, intestinal cæca reaching near the hind end and forming characteristic loops behind the ventral sucker, dorsal sinistral position of the genital opening behind the acetabulum near or a little in front of the middle of body length, testes two in number with the ovary between them, well developed cirrus sac situated in front of the anterior testis with the vesicula seminalis outside it near the right intestinal cæcum, a stout eversible cirrus, well developed muscular metraterm and short uterus containing a single large ovum with one or two polar filaments situated in front of the ovary, strongly developed vitellaria overlapping the cæca and uniting mesially behind the acetabulum and posterior testis leaving free the genital field, and a small but prominent excretory bladder with a short median stem, two anterior cornua and lateral lobes, situated at the hind end.

The important features in which *C. odhnerensis* differs from *C. lyssimus* and which entitle it to the rank of a different species are:—

- (1) Shape of the body; elongated and narrow in *C. odhnerensis*, much broader behind ventral sucker with a broad posterior end in *C. lyssimus*.
- (2) Absence of papillæ in the body wall.
- (3) Oral sucker larger than ventral sucker; reverse condition in *C. lyssimus*.
- (4) Intestinal cæca not undulating behind posterior testis.
- (5) Testes irregularly lobed.
- (6) Characteristic shape of ovary; flask-shaped in *C. odhnerensis*, somewhat triangular or conical in *C. lyssimus*.
- (7) Crescentic shape of cirrus sac; retort shaped in *C. lyssimus*.
- (8) Shape of protruded cirrus; stick-shaped in *C. odhnerensis*, broad and flattened with a narrow base in *C. lyssimus*.
- (9) Anterior limit of vitellaria, intestinal bifurcation in *C. odhnerensis*, posterior border of acetabulum in *C. lyssimus*.

(10) Character of the ovum.

(11) Main stem of excretory bladder a little longer, with one pair of small rather inconspicuous lateral lobes.

### Diagnosis of the Genus *Coeuritrema* N. G.

Haplotremineæ: Hermaphrodite distome blood flukes; delicate musculature.

Body elongated, narrow or broad behind ventral sucker; size very small; body wall with or without small papillæ; oral sucker protrusible; ventral sucker protractile and retractile, situated at about one third body length from anterior end. Pharynx absent; œsophagus long surrounded by salivary gland cells which are numerous near its posterior extremity; intestinal bifurcation close in front of ventral sucker; intestinal cæca reaching a little in front of hind end and forming characteristic loops behind ventral sucker in region of genital opening, left cæcal loop more pronounced. Genital opening dorsal, sinistral close behind ventral sucker near middle of body length close outside left cæcum. Testes two in number with ovary between them, situated in third quarter of body, intracæcal and usually lobed; anterior testis lying to the right, immediately behind cirrus sac and close in front of ovary; posterior testis median, immediately behind ovary and receptaculum seminis. Ovary conical or flask-shaped, situated to the left with transverse vitelline ducts close behind it; vitelline reservoir in front of transverse ducts. Receptaculum seminis pear-shaped, rounded or oval situated to the right near right cæcum, immediately in front of posterior testis. Cirrus sac large, muscular and crescent shaped or retort shaped with a concavity in its right wall, situated immediately in front of anterior testis. Vesicula seminalis small, external, and to the right side near right cæcum opposite to the cirrus sac. Cirrus well developed, without spines. Metraterm well developed and muscular, situated in front of ovary and to the left side of anterior testis and cirrus sac. Uterus short, indistinguishable from metraterm except by the absence of musculature, containing a single large ovum bearing filaments at ends. Vitellaria well developed lateral, overlapping the cæca, uniting mesially behind ventral sucker in the region between it and genital opening, and behind posterior testis, leaving entirely free the genital field. Excretory bladder small and tubular at hinder end with a short median stem provided with one or two pairs of lateral lobes and dividing near blind ends of cæca into two small but prominent cornua.

Habitat: Ventricle of heart.

Host: Water tortoises, *Lissemys punctata*. Locality: Allahabad, India.

*Type species*.—*Coeuritrema lyssimus* sp. n.

### Previous Work on the Blood Flukes of the Family Spirorchidæ Stunkard, 1921

The family Spirorchidæ contains the blood flukes of turtles assigned to the following genera:—*Hapalotrema* Looss, 1899, *Spirorchis* MacCallum, 1918 syn. *Proparorchis* Ward, 1921, *Henotosoma* Stunkard, 1923, *Hæmatotrema* Stunkard, 1923, *Hapalorhynchus* Stunkard, 1923, *Vasotrema* Stunkard, 1926, *Unicæcum* Stunkard, 1927, *Spirhapalum* Ejsmont, 1927 and *Diarmostorchis* Ejsmont, 1927. Stunkard in 1921 divided this family into two sub-families, Spirorchinæ Stunkard and Hapalotremiæ Stunkard which he defined. In the former sub-family have been included the genera *Spirorchis*, *Henotosoma*, *Hæmatotrema*, and *Unicæcum*; in the latter, the genera *Hæmatotrema*, *Hapalorhynchus* and *Vasotrema*. *Spirhapalum* and *Diarmostorchis* are considered as connecting genera between the two sub-families by Ejsmont, who has consequently expressed an opinion of dropping the sub-families.

Looss in 1899 created the genera *Hapalotrema*, *Bilharziella* and the family Schistosomidæ. He pointed out, in the course of discussion about these genera, that the points of resemblance between them do not indicate a close relationship, but merely adaptations due to a constantly similar environment. Odhner in his memorable paper in 1912 included *Hapalotrema* in the sub-family Liolopinæ of the family Harmostomidæ, which he created with diagnosis. He derived the Bilharziidæ, now known as the Schistosomidæ from the Liolopinæ through such forms as indicated by the following type series:—*Liolope*, *Hapalotrema*, *Bilharziella*, *Ornithobilharzia*, *Bilharzia*. Ward (1921), on the basis of a close similarity between *Proparorchis* and *Hapalotrema*, removed the latter genus from the Liolopinæ and included it with his *Proparorchidæ* in his family *Proparorchidæ*, now well known as the Spirorchidæ. After emphasising the points of difference between *Spirorchis* and *Hapalotrema* he concluded that if the posterior region in the latter genus be reduced by the failure of the posterior testis to develop with the correlated cessation of growth in the posterior of the worm, the distome would show a condition of reproductive organs with the ovary and its associated genital ducts near the hind end as met with in the genus *Spirorchis*. Stunkard in 1921 accepted the main idea advanced by Ward about the close relationship of the two genera of blood flukes of turtles, i.e., *Spirorchis* and *Hapalotrema*, which he included in the family Spirorchidæ named after the type genus *Spirorchis* on the basis of priority. He also divided this family into two sub-families as mentioned above. Ejsmont in 1927 while describing his new genus and species *Spirhapalum polesianum* assigned *Spirorchis blandingi* MacCallum to a new genus *Diarmostorchis*, as it differed from all the other species of the genus *Spirorchis* in possessing the hindmost testis behind the ovary. He considered this genus to be a connecting link between the blood flukes of American and European turtles. As the genera *Spirhapalum* and *Diarmostorchis* combine in themselves the characters of the Spirorchinæ and Hapalotremiæ, he expresses the opinion of dropping the sub-families. According

to the relative position of the ovary and the testes Ejsmont has shown an ascending series of genera with a gradual transformation from *Spirorchis* having about 10 preovarian testes to *Hapalorhynchus* having only two testes with the ovary between them, and traces the forward position of the genital opening with the correlated ducts and the forward position of the ovary in *Hapalotrema*, *Hapalorhynchus* and the Schistosomidæ from their position near the hind end in *Spirorchis* through such transition genera as *Diarmostorchis* and *Spirhapalum* as the result of their gradual displacement towards the anterior end. In the final stages, *i.e.*, in *Hapalorhynchus* and Schistosomes where the culminating point is reached, the genital ducts have quitted their primitive position behind the testes and at about the level of the ovary, crossed the latter and reached the anterior testis with the genital opening shifted still more forwards, *i.e.*, in front of the latter.

Stunkard in 1921 and 1923 had expressed the opinion that the Spirorchidæ occupies an intermediate position between the Schistosomidæ and the Aporocotylidæ and that the Schistosomes are to be derived through them from the Aporocotylidæ, rather than from the Harmostomidæ as maintained by Odhner. Poche (1925), however, does not agree with Stunkard's view saying that the absence of suckers and the presence of follicular testes in the Sanguinicolidæ and the Aporocotylidæ warrant against it. In 1926 Stunkard created the new genus and species *Vasotrema amyda* and in 1928 added two more species, *i.e.*, *Vasotrema attenuatum* and *Vasotrema robustum* to it. In 1927 he created the genus *Unicaecum*, including it in the sub-family Spirorchinæ and emended the sub-family and family diagnosis. He also pointed out that *Unicaecum* suggested the creation of a new sub-family for it and that sooner or later a new classification of the family may be deemed necessary. In 1928 in his paper on the new observations on the genus *Vasotrema*, he gave a review of the knowledge of the blood flukes and accepted Ejsmont's conclusions about *Diarmostorchis* and *Spirhapalum* as the connecting genera between the sub-families Spirorchinæ and Hapalotremiæ. He also stated that the study of the genus *Vasotrema*, which possesses one large testis situated behind the ovary confirms entirely the theory about the phylogenetic relationships of blood flukes propounded by him and Ejsmont, and pointed out that the relative position of the genital organs demonstrates that no other family of trematodes presents such great morphological variations as the Spirorchidæ in the number of suckers, in the form of the œsophagus and digestive cæca, in the number and position of the testes, in the form and situation of the ovary, in the presence or absence of Laurer's canal, Mehli's gland and cirrus sac and finally in the position of the vesicula seminalis and the genital pore. The existence of intermediate forms between the whole connected series of genera, however, shows that they all belong to one and the same family.

From the above historical account it would be clear that there are two views about the evolution of the families of blood flukes, one expressed by Odhner, *i.e.*, the Schistosomidæ are derived from the Liolopinæ of the Harmostomidæ through

*Hapalotrema*, and the other put forward by Stunkard and Ejsmont that the Spirorchidæ stands in an intermediate position between the Schistosomidæ and the Aporocotylidæ and that the Schistosomes are evolved through them from the Aporocotylidæ rather than from the Harmostomidæ. In the opinion of these authors the sub-family Spirorchinæ represents the primitive condition of reproductive organs of the family Spirorchidæ.

We may so far anticipate our own conclusions arrived at in the subsequent discussion as to say, that the Hapalotremiæ of the Spirorchidæ forms the central stock, from which are evolved on the one hand the Schistosomidæ and on the other the degenerate blood flukes of the families Aporocotylidæ and Sanguinicolidæ; and that the genus *Coeuritrema* has relations on the one hand with the Liolopinæ and on the other with *Hapalotrema*, *Hapalorhynchus*, *Vasotrema* and the Schistosomidæ.

### Discussion on the Systematic Position of the Genus *Coeuritrema* and the Relationships of the Families of Blood Flukes.

It will be apparent from the description of the species and the generic diagnosis that *Coeuritrema* belongs to the family Spirorchidæ and the sub-family Hapalotremiæ, which it resembles in the following features:—

1. Presence of protrusible oral and ventral suckers.
2. Acetabulum situated near the end of anterior third of body.
3. Absence of pharynx.
4. Long œsophagus surrounded by salivary gland cells which are densely crowded near the intestinal bifurcation; intestinal cæca reach near hinder end.
5. Testes two in number with the ovary between them as in *Hapalorhynchus*. In *Hapalotrema* the two testes are divided into a large number of follicles so as to form two testicular masses, one in front of the ovary and the other behind it. In *Vasotrema* the anterior testis is absent, i.e., suppressed, and the posterior large and much lobed.
6. Genital pore situated to the left on the dorsal side, behind ventral sucker about the middle of body length. In *Vasotrema*, however, it is sinistral and ventral and not dorsal.
7. Ovary, receptaculum seminis, Laurer's canal and ootype situated near or a little behind middle of body.
8. Muscular cirrus sac present. *Hapalorhynchus* is the only genus in the sub-family, in which the cirrus sac is absent.
9. Protrusible cirrus well developed, absent in *Hapalorhynchus*.
10. Vesicula seminalis outside cirrus sac.
11. Uterus short; muscular metraterm well developed. Only one ovum present in uterus or proximal part of metraterm and discharged singly.
12. Ovum large with filaments at ends.
13. Vitellaria well developed, lateral and medial to the cæca throughout most

of their course. In *Coeuritrema* and *Vasotrema robustum* they unite mesially behind ventral sucker and posterior testis (in the latter only one testis present).

14. Excretory vesicle short and tubular situated near hind end with a short median stem dividing into two cornua or lobes much behind posterior testis.

There is a close resemblance amongst the various genera of the sub-family Hapalotremiæ, which we following Stunkard sharply separate from the Spirorchinæ. We do not agree with Ejsmont that as *Spirhapalum* resembles in one or two features the genus *Hapalotrema*, the division of the Spirorchidæ into sub-families should be dropped. The presence of one testis follicle behind the ovary and the presence of a ventral sucker in *Spirhapalum* should not be considered as features of sufficient importance so as to give it the position of an intermediate genus between the two sub-families. Though the presence of two testes or testicular masses, one in front and the other behind the ovary, is one of the characteristic features of the Hapalotremiæ, the topography of all the genital organs taken together in *Spirhapalum* resembles closely that of the Spirorchinæ, and we are inclined to think that the presence of one testis follicle behind the ovary is an example of reversion rather than a step towards the evolution of the arrangement and position of the testes met with in the Hapalotremiæ. The sinistral dorsal or ventral position of the genital opening about the middle of body length and the forward position of the ovary with its associated ducts and the cirrus sac near or a little in front of the middle of body are important features of the Hapalotremiæ, to which due importance should be given in deciding this question. Stunkard has pointed out that the number and position of the testes are very variable in the family, and we go a little further and say that they show variability even in the two sub-families. In *Vasotrema*, which Stunkard includes in the Hapalotremiæ there is only one large testis present behind the ovary; in *Unioæcum*, which he includes in the Spirorchinæ there is one large testis present in front of the ovary. In *Hapalotrema* the two testes separated by the ovary are divided to form two follicular masses, whereas in *Hapalorhynchus* and *Coeuritrema* they are not divided into follicles. *Spirhapalum* and *Diarmostorchis* possess the ovary with its associated ducts, genital opening and the cirrus sac near the hind end as in *Spirorchis* and therefore should be included in the Spirorchinæ, which comprises both monostomes and distomes. The presence of a ventral sucker in *Spirhapalum* should also not be considered as a great distinction from the Spirorchinæ, as in a number of species very closely related to *Spirorchis*, which I shall describe in a subsequent paper the ventral sucker is present; and, moreover, it is well known that the presence or absence of a ventral sucker by itself is not to be considered as a feature of more than specific or generic rank.

Among the Hapalotremiæ *Coeuritrema* shows in itself some characters of all the three well-known genera of the sub-family as has been pointed above. From *Hapalotrema* it differs in the intestinal cæca forming a characteristic loop behind the ventral sucker in the region of the genital opening, testes not divided into

follicles so as to form two testicular masses one in front and the other behind the ovary and the genital opening situated in front of the gonads as in *Hapalorhynchus* and not behind the anterior testes in level with the ovary. In *Vasotrema* also the genital pore lies in level with the ovary, but the anterior testis or testicular mass is absent in this genus. In *Hapalotrema* and *Vasotrema* the vesicula seminalis lies in the median plane in front of the ovary, whereas in *Coeuritrema* and *Hapalorhynchus* it lies in front of all the gonads, smaller and to the right side in the former, median and much larger in the latter. *Hapalorhynchus* resembles *Coeuritrema* in the number of the testes and their position one in front and the other behind the ovary, position of the genital opening and the vesicula seminalis in front of the gonads, in the characteristic loop formed by the left intestinal cæcum, the extent of the vitellaria and the hosts being fresh water turtles, but the enormous development of the prostate and the absence of the cirrus sac and the cirrus distinguishes it from the latter. In *Coeuritrema* the cirrus sac is directed forwards with the basal end lying in front of the anterior testis, whereas in *Vasotrema* and *Hapalotrema* it is directed backwards, a condition which is also met with in the genus *Bilharziella* among the Schistosomidæ. The vesicula seminalis is small and lies to the right side of the cirrus sac in *Coeuritrema*, but it is large and median in all the other genera of the Hapalotremiæ and in *Bilharziella*. In *Liolope* also the vesicula seminalis, though large, lies to the right side near the right cæcum. The medial union of the vitellaria behind the ventral sucker and posterior testis in *Coeuritrema* resembles closely that in *Vasotrema robustum*.

Odhner has discussed the affinities of *Hapalotrema* with *Liolope* and *Bilharziella* and considers it to form a connecting link between the families Harmostomidæ and Schistosomidæ. The close affinities of *Coeuritrema* with *Hapalotrema* have been already pointed out, and now I contend that *Coeuritrema* stands much nearer *Liolope* than *Hapalotrema*.

The essential features in which it resembles *Liolope* are the following :—

- (1) Suckers well developed ; ventral sucker usually larger.
- (2) Testes two in number with the ovary between them, situated in posterior half of body, and not divided into follicles.
- (3) Genital opening in front of gonads, near or a little in front of middle of body and strongly shifted to the left side.
- (4) Cirrus sac well developed and situated behind ventral sucker and in front of anterior testis.
- (5) Vesicula seminalis external and to the right side of cirrus sac near right intestinal cæcum in front of gonads.
- (6) Metraterm well developed.
- (7) Excretory system.
- (8) Large size of ovum.

It seems that all these features were present in the ancestral blood fluke related to *Liolope*, when it took to a life in the blood of the ventricle of the heart and arteries of an amphibian or reptilian host. *Coeuritrema* is the only genus in the Hapalotremiæ which possesses all these characters in addition to those which it holds in common with the other genera of the subfamily as adaptations due to a common environment such as the absence of pharynx, long oesophagus surrounded by salivary gland cells and lined internally with cuticle, delicate body with scantily developed musculature, short female duct and formation and extrusion of ova one by one. We think that in the ancestral blood fluke the cirrus sac was laterally directed towards the sinistral genital opening with the vesicula seminalis to its right side as in *Liolope*. From this condition we can derive on the one hand the forwardly directed cirrus sac of *Coeuritrema* with the genital opening in front and on the other the backwardly directed cirrus sac of *Hapalotrema*, *Vasotrema* and male *Bilharziella*. It is interesting to note that *Coeuritrema* resembles male *Bilharziella* more closely than *Hapalotrema*, though it has not got the testes divided into follicles. The two genera resemble remarkably in the position of the genital opening behind the ventral sucker to the left side a little in front of the middle of body. The mesial bending of the intestinal cæca behind the ventral sucker and the posterior testis in *Coeuritrema* represents in an incipient condition the formation of the posterior cæcum by the caudal union of the intestinal cæca either in front of the testes or behind them, which is typical of the family Schistosomidæ. In *Bilharziella* the caudal fusion of the cæca has taken place behind the genital opening, i.e., in front of the testes, while in *Ornithobilharzia* it has taken place behind the testes a little distance in front of the hinder end, equivalent to the region behind the posterior testis in *Coeuritrema*, where the cæca bend so much mesially towards each other that in contracted specimens they sometimes meet together in the median line. The formation of mesial loops by the cæca behind the ventral sucker and the posterior testis certainly throws some light on the formation of the caudal cæcum in the Schistosomidæ.

There is no doubt that the ancestor of the Schistosomidæ, though it closely resembled *Coeuritrema* had its testes divided into follicles somewhat like those of *Hapalotrema* and this tendency was strongly inherent in its immediate ancestors. With the separation of sexes, which took place when the ancestral Schistosomes inhabited the portal and mesenteric veins of homothermal vertebrates i.e., birds and mammals, the follicular testes formed together one mass, which in some genera became located in front of the caudal union as in *Ornithobilharzia* and in the other behind it as in *Bilharziella*. The strongly muscular and eversible ventral sucker and well developed metraterm of *Coeuritrema* and the other Hapalotremiæ confirm the above conclusions about these relationships. The presence of papillæ in the body wall of *O. lyssimus* recalls the same in some species of the genus *Schistosoma*. In the Bilharziellinæ the uterus is short and contains a single ovum as in the Spirorchidæ and the gynæcophoric canal is absent or imperfectly formed. It seems



apparent then that the Bilharziellinæ are derived from the Hapalotremiæ through an ancestral form closely related to *Coeuritrema*. From a form closely related to *Bilharziella* we can derive *Ornithobilharzia*, *Austrobilharzia* and *Heterobilharzia* in which the cirrus sac is present and the uterus contains only one ovum at a time. The suckers are also well developed in these genera. From forms closely related to them can be derived the genus *Schistosoma*, which has lost the cirrus sac and in which the genital pore lies in the median line, the number of testes is relatively small and the uterus contains a large number of ova.

The origin of the Spirorchinæ can be traced from a form somewhat like *Hapalotrema*, in which the anterior testicular mass developed preponderantly keeping pace with the much greater rate of growth of the part of body in front of the ovary so that the latter with the associated ducts and the hinder testis (not divided into follicles) came to occupy a position near the hind end of the body as in *Spirhapalum*. The form from which the Spirochinæ has arisen, however, differed from *Hapalotrema* in the important point that while the anterior testis was divided into follicles, the posterior testis remained undivided. The culminating point was reached when the posterior testis became entirely suppressed so that the ovary with its associated ducts came to lie near the hind end as in *Spirorchis*.

That this is likely is borne out by the fact that in *Vasotrema* the anterior testis is suppressed and the posterior testis considerably increased in size. It seems that *Spirhapalum* stands near the end of a series of changes in the backward shifting of the ovary and its correlated ducts as we find in the genus *Spirorchis*. The Hapalotremiæ of the Spirorchidæ forms the central stock, from which are evolved on the one hand the Spirorchinæ and on the other the Schistosomidæ and *Coeuritremæ* represents a form closely related to the ancestor through which the Hapalotremiæ are derived from the Liolopinæ. It is well known from the study of different groups of animals that evolution does not take short straight cuts along one line as Stunkard and Ejsmont contemplate according to their theory of the phylogenetic relationships of blood flukes in an ascending series from the Aporocotylidæ through the Spirorchinæ to the Hapalotremiæ and the Schistosomidæ. On the other hand ample evidence is afforded from the study of various groups of animals that evolution always takes place in divergent lines from a central generalised type and this we maintain applies with equal emphasis in the case of the families of blood flukes. We should not expect our ancestral blood fluke to possess more than two testes, as this is the most usual number for the order Digenea. The division of these two testes, into follicles should be considered as a secondary condition which is met with in a few other families besides the families of blood flukes, as for instance, in some genera of the Pronocephalidæ. Among all the sub-families and families of blood flukes Hapalotremiæ is the only subfamily in which two genera i.e., *Coeuritrema* and *Hapalorhynchus* show the primitive number of testes; besides in the third genus i.e., *Hapalotrema* these two testes have become divided into follicles. In the spirorchinæ and the

Aporocotylidæ a large number of testes *i.e.*, testis follicles are present, which is certainly a secondary and not a primary condition, it is, therefore, but natural for us to consider this latter condition as having been evolved from the condition of the testes in the Hapalotreminæ.

In the same way we can derive from the ancestral form closely related to *Coeuritrema* and *Hapalotrema* through a form like *Spirorchis* the family Aporocotylidæ and the more degenerate Sanguinicolidæ, which we shall discuss in a subsequent paper.

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### Explanation of Plates and Key to Lettering used in Figures

Figures 1-6. *Coeuritrema lyssimus*.—

1. Dorsal view of a specimen.
2. Microphotograph of entire mount. Dorsal view.  
Leitz Eyepiece X; Leitz Objective 3, 10 X.
3. Microphotograph of horizontal longitudinal section showing genital organs. Leitz Eyepiece O; Zeiss Objective 40 D.
4. Microphotograph of transverse section through ventral sucker. Leitz Eyepiece 3; Leitz Objective 6lg, 45 X.
5. Microphotograph of transverse section through genital opening showing everted cirrus, terminal part of cirrus sac, metraterm and intestinal cæca.  
Leitz Eyepiece 3; Leitz Objective 6lg, 45 X.
6. Microphotograph of transverse section through cirrus sac, metraterm and vesicula seminalis.  
Leitz Eyepiece 3; Zeiss Objective 40 D.

Figure 7. *Coeuritrema odhnerensis*.

7. Microphotograph of entire mount. Dorsal view.  
Leitz Eyepiece 3; Leitz Objective 3, 10 X.

a t., anterior testis; c.s., cirrus sac; ex.b., excretory bladder; i.c., intestinal cæcum; l.i.c., left intestinal cæcum; l. l.i., loop of left intestinal cæcum; m., metraterm; o.s., oral sucker; œs, œsophagus; ov., ovary; p.t., posterior testis; r.s., receptaculum seminis; r.i.c., right intestinal cæcum; s.g., salivary gland cells; t.c.s., terminal part of cirrus sac; v.s., ventral sucker; ves s., vesicula seminalis; vit., vitellaria.

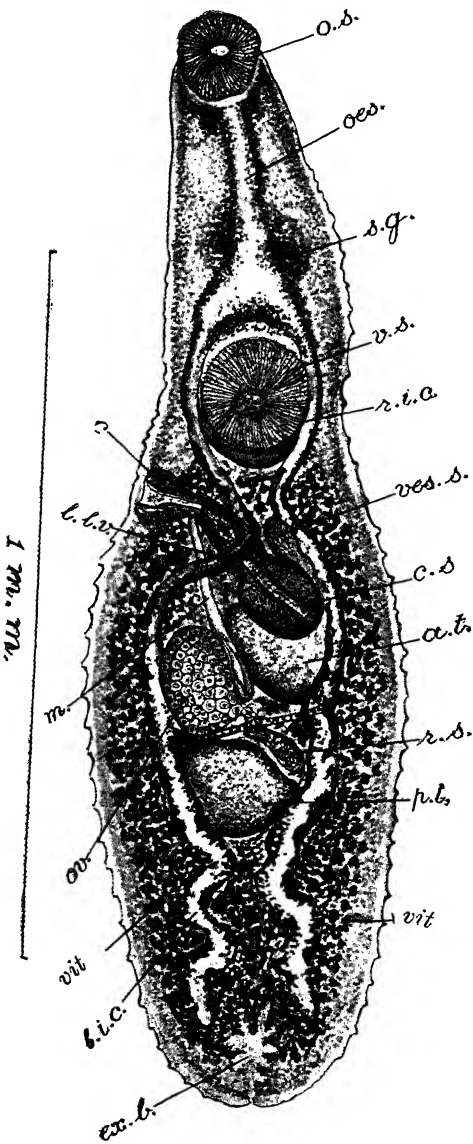


Fig. 1

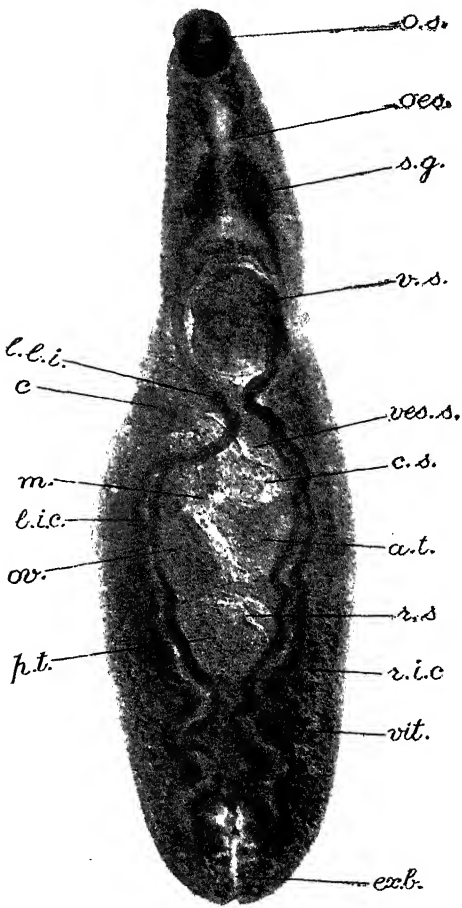


Fig 2

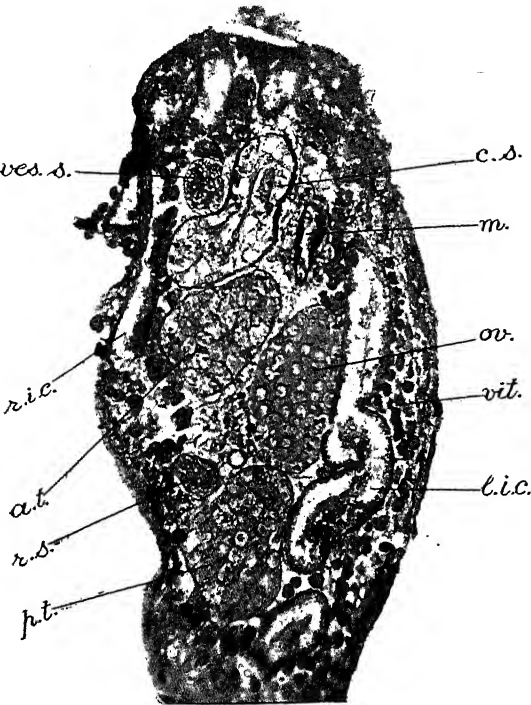


Fig 3



Fig 4

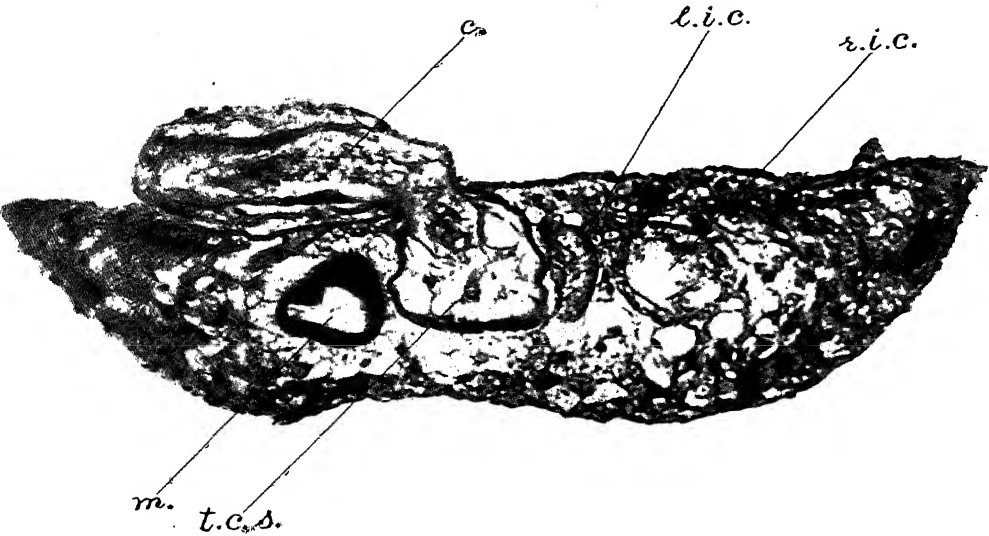


Fig 5

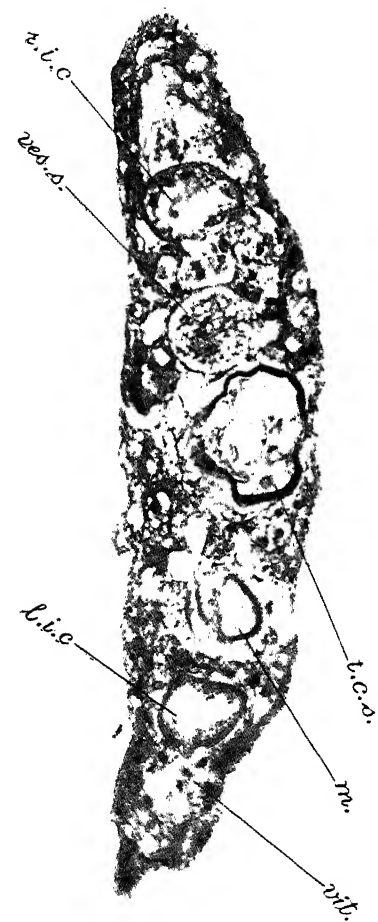


Fig. 6

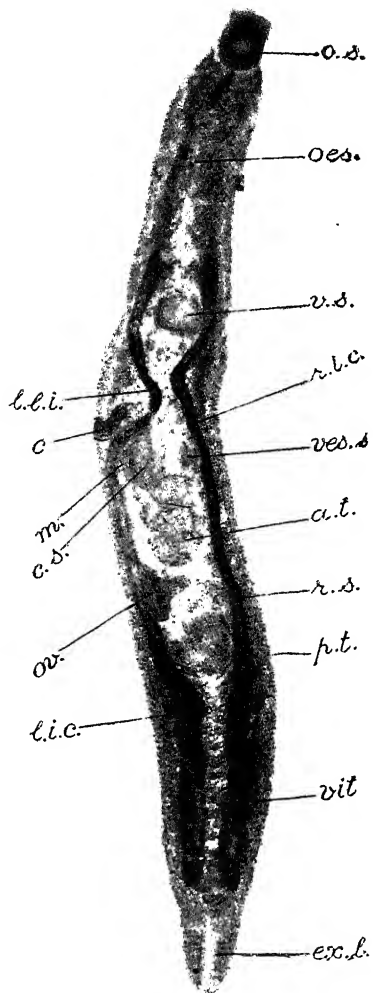


Fig. 7

# CONCLUSIONS ON THE STRENGTH AND NATURE OF BINDING FROM THE CONTINUOUS ABSORPTION SPECTRUM

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In recent years a large number of calculations on the Heat of Dissociation particularly of diatomic molecules, were made from the structure of the absorption and emission band spectra. The calculations can be carried out with great exactness if the spectral position of band convergence can be correctly determined. If light having the frequency corresponding to this convergence frequency be absorbed then we add to the molecule an amount of energy which is equivalent to that required for the electron-spring together with as much oscillation energy as is necessary for just disrupting the molecule into its constituent atoms, so that, after separation, the constituents have no kinetic energy relative to each other. If the absorption extends only to a part of the band-spectrum, and not up to the convergence limit, then the position of the band convergence can be extrapolated more or less exactly from the frequencies of the band heads. If, on the other hand, the coupling relations are such that, together with the energy necessary for the electron spring, a somewhat larger amount of oscillation energy is also added than what is necessary for dissociation, then we observe a continuous spectrum, and from its position we can obtain the maximal value of the heat of dissociation. Owing to the fact that alkali halides in the gaseous state give us such values which agree with values obtained independently the utility of the process has been over-estimated.

Even in the first application of the considerations regarding the significance of the continuous absorptions of the alkali halides,<sup>1</sup> the authors discussed the grounds due to which the procedure may give inaccurate results. Clearly these



results cannot be taken as sufficiently accurate and now-a-days they can be formulated in a more precise way. In the following, therefore, we want to define our position in respect to this question by using the experimental results of other authors working in the field. It depends very closely on the problem whether we have to deal with ionic or atomic binding. On this complex question results have already been given in the abovementioned works of the author<sup>2</sup>, but these are to be partly extended and partly curtailed. This shall be done in the following:—

At the time we wrote our first series of papers such molecules were defined as ionic molecules in which by following the oscillation terms of the ground state up to the convergence limit they can be shown to decompose into ions. If they decompose into atoms we call them as atomic molecules. The amount of energy required for splitting up into ions is always greater than that for splitting into neutral atoms. Therefore the potential energy curves for these two states intersect. The intersection of the curves can under certain circumstances cause some ambiguity when we want to follow up the oscillation systems to convergence, and therefore sometimes the distinction between atomic and ionic molecules may turn out to be illusory. But no such case is known up to this time, and theoretically, it is not expected as well.

Up to this time these definitions have been found to be unambiguous. This classification does not coincide with the division of molecules into homopolar and heteropolar groups. Ionic molecules are always heteropolar, the atomic

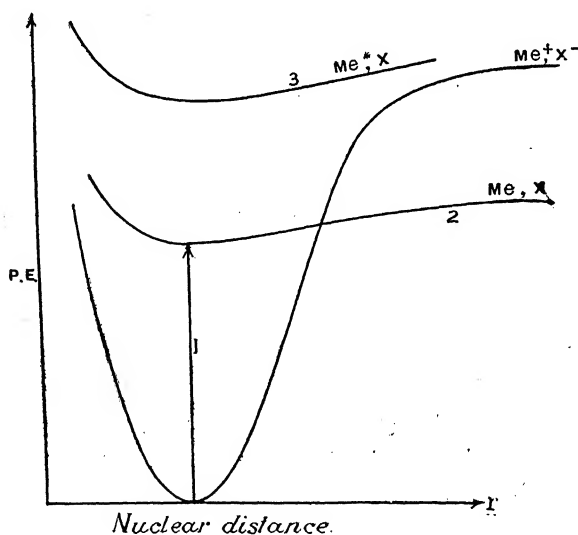


Fig. 1

molecules, on the other hand, may sometimes possess some electric moment and may be at other times nonpolar.

As is clear from the above potential-energy curves the state of an atom-molecule always represents an excited state of ionic molecule when transition takes place from the fundamental state to the first excited state. Due to absorption of light, then, in the limit, we have dissociation into normal atoms (Arrow 1). The authors have designated the occurrence of such transitions as a criterion for ionic binding. It is now held that this deduction is limited in its application for Heitler and Herzberg<sup>3</sup> have shown that there are exceptional cases in which the fundamental state of a molecule is formed out of a normal and an excited atom. Therefore an excited state of the molecule may consist of normal atoms. Further, Brown<sup>4</sup> has shown, in a series of work on the absorption spectra of halogens, that in the case of diatomic halogens which are to be regarded as atomic molecules, optical decomposition into two atoms takes place very feebly. The above criterion, therefore, represents a necessary, but not a sufficient condition for the case of an ionic binding. As a typical limiting case of pure ionic binding we can take the case in which the binding forces are caused entirely by coulombian forces. That is, forces due to resonance interaction are not present, the polarisation having only a very small influence on the binding. Then a transition from the fundamental state of the ionic molecule to the state of the atomic molecule, which is equivalent to the transfer of an electron from kation to the anion- will completely destroy the coulombian binding and, with that, practically the whole binding force will disappear. On account of this reason we have a part of the potential energy curves 2 and 3 running almost parallel to the abscissa. That is why the minimum is not at all prominent in the case of ionic molecule. If the atom molecules are bound by forces of resonance interaction then the excited molecules show curves with very pronounced minima, and with a steep left hand side branch indicating repulsive force.

The fact that the curve for the excited alkali halides rise from a flat form almost perpendicularly over the minimum of the ground state, causes, as has been discussed already, the occurrence of the continuous absorption spectra, which stretch over relatively short wavelength regions.<sup>5</sup> A well-defined long wavelength limit does not exist and is not to be expected even when we consider the part of the spectra which is produced by the deepest oscillation state of the molecule. If we want to use the limiting long-wavelength frequency of the continuous absorption we have to utilise the point from which a steep rise of the absorption coefficient begins and we obtain only an upper value for the corresponding heat of dissociation. We can draw conclusions from the part of the curve of absorption coefficients running asymptotically on the longer side of this limit when the absorption by the oscillation levels belonging to the fundamental state can be quantitatively taken account of. But even when these not very easy calculations are taken into account it is unjustified to give values of the heat of dissociation correct up to the tenth part of a k. cal, as we very often find in literature. Further, out of an extremely faint tail of the long wavelength side of the absorption curves, we can draw no conclusion on the nature

of binding, as Rollefson and Booker<sup>6</sup> as well as Dutta<sup>7</sup> had done in the case of hydrogen halides.

These authors believe that our former reasonings for regarding the hydrogen halides as atom molecules\* are contradicted by the fact that when the gas pressure is very high, a feeble absorption is observed up to a wavelength, which is smaller than the energy of excitation of the hydrogen halides to a normal hydrogen and excited halogen. Even when (what does not seem to be probable according to the above considerations) an extremely feeble absorption would lead from fundamental states to normal atoms, we have at most an analogy to the atom-molecules of halogens, but not an analogy of that of the ionic molecules of alkali halides.

The continuous absorption of 3, 4, 5 atomic molecules, and whether in their compositions, they can be regarded as ionic or atomic molecules on the basis of their spectra, have been investigated in a series of papers by Saha<sup>8</sup> and his co-workers. It has been found that from the long wavelength limit we always calculate a longer value of energy than what is necessary for the separation of the normal atom from the normal-rest. This behaviour is not in contradiction to the above conception. Even in the case of a tri-atomic ionic molecule, which can be represented by the formula  $X^- Me^{++} X^-$ , with electron spring from one  $X^-$  to the kation the binding of this atom ceases, and simultaneously the coulombian attraction forces between the second anion and kation are strongly altered, so that the rest  $X^- Me^+$  remains in a strongly oscillating state. An analogous condition holds in a stronger measure also for the ionic molecules with larger atom numbers. Conclusions on the energy of dissociation and on the nature of binding cannot therefore be drawn only out of the long wavelength limit of continuous absorptions of polyatomic molecules without further work.

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\* The principal ground for classifying the alkali halides as ionic molecules was due to their having two maxima in the absorption spectra separated by a distance corresponding to the energy of excitation of the halogen constituents.

## NORMAL FREQUENCY SPECTRA

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Communicated by Prof. M. N. Saha,

Received, January 23, 1933.

In the analysis of a complex spectrum it is often necessary to find out pairs of lines whose frequencies have a constant difference. The usual method of choosing two suitable lines, finding their frequency difference, and searching for other pairs having that difference, though quite exhaustive and accurate, is lengthy, especially when the correct constant-difference to be searched for is not known. Another method is to plot the frequencies along a line. The intensity of any spectral line might be represented by the length of a line drawn perpendicular to the previous line from the corresponding point. To search for constant frequency differences then is to search for equidistant lines. This might be done by means of a scale, or, more conveniently by sliding one such chart over another and noting coincidences. The rough idea of intensities is also a guide in the selection of pairs.

It would be much more convenient if an enlarged picture of the spectrum could be had on a normal frequency scale. In a paper on "The reproduction of prismatic spectrum photographs on a uniform scale of wave-lengths" Fowler and Eagle<sup>1</sup> have noted that the method indicated in the paper could also be applied to produce normal frequency spectra, but they gave no details. The details for this as applied to both prismatic and grating spectra are given below.

Fig. 1 is reproduced from Fowler and Eagle's paper, in which it is described as follows :—

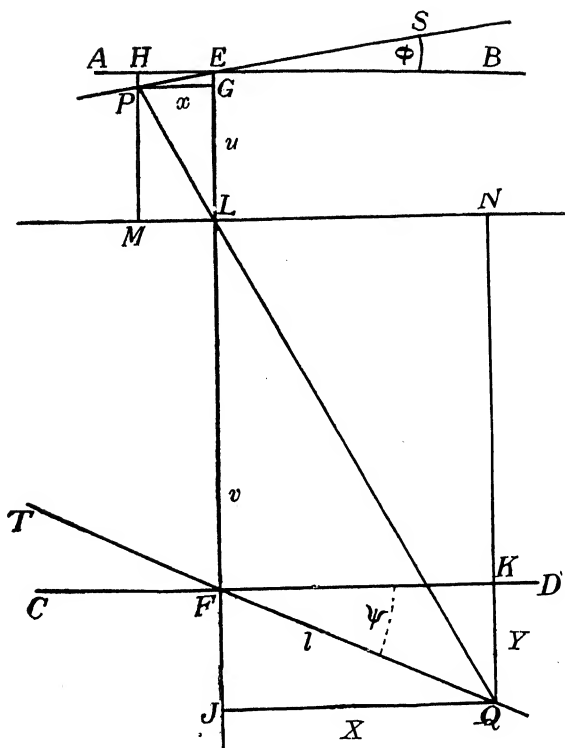


Fig. 1

"Let  $L$  be a lens which will bring equidistant points lying on a plane  $AB$  perpendicular to the axis of the lens, into focus as a system of equidistant images on another plane  $CD$ . In the diagram let  $EL=u$ ,  $FL=v$ ,  $PG=x$ ,  $PH=y$ ,  $QJ=X$ ,  $QK=Y$ ,  $\angle SEB=\phi$ ,  $\angle QFD=\psi$ ,  $PE=s$  and  $QF=l$ ."

The following results can be easily derived as shown in the paper:

$$v = \frac{fu}{u-f} \quad \dots \quad \dots \quad \dots \quad \dots \quad (1)$$

$$\frac{Y}{X} = \frac{y}{x} \cdot \frac{v}{u} \quad \dots \quad \dots \quad \dots \quad \dots \quad (2)$$

From (2) since  $y/x$  is constant along  $PS$ ,  $Y/X$  is also constant, *i.e.*, all points lying on  $PS$  will be brought into focus on another straight line  $QT$ ;

$$\tan \psi = \frac{v}{u} \tan \phi \quad \dots \quad \dots \quad \dots \quad \dots \quad (3)$$

$$l = \frac{fks}{u-f-s \sin \phi} \quad \dots \quad \dots \quad \dots \quad \dots \quad (4)$$

where  $K = \sqrt{(\cos^2 \phi + \frac{v^2}{u^2} \sin^2 \phi)}$

$$\frac{dl}{ds} = \frac{fk(u-f)}{(u-f-s \sin \phi)^2} \quad \dots \quad \dots \quad \dots \quad (5)$$

If we have a prismatic spectrum on the plate PS for which the wavelength at a distance  $s$  from the centre of the plate is given by the Cornu-Hartmann formula,

$$\lambda = \lambda_0 + \frac{c}{s+s_0}, \quad \text{we have, } \frac{d\lambda}{ds} = -\frac{c}{(s+s_0)^2}$$

the wave-number  $\nu = \frac{10^8}{\lambda} \quad \therefore \frac{d\nu}{d\lambda} = \frac{-10^8}{\lambda^2}$

or substituting for  $\lambda$ , 
$$\frac{d\nu}{d\lambda} = -\frac{10^8(s+s_0)^2}{\{\lambda_0(s+s_0)+c\}^2}$$

Hence, for the spectrum on QT we have,

$$\begin{aligned} \frac{d\nu}{dl} &= \frac{d\nu}{d\lambda} \cdot \frac{d\lambda}{ds} \cdot \frac{ds}{dl} = -\frac{10^8(s+s_0)^2}{\{\lambda_0(s+s_0)+c\}^2} \times \frac{-c}{(s+s_0)^2} \div \frac{fk(u-f)}{(u-f-s \sin \phi)^2} \\ &= \frac{10^8 c}{fk(u-f)} \left\{ \frac{u-f-s \sin \phi}{\lambda_0(s+s_0)+c} \right\}^2 \quad \dots \quad (6) \end{aligned}$$

Now  $d\nu/dl$  gives the variation of wave-number with respect to length along the enlargement. If it is required that each unit length of the enlargement should correspond to a fixed number of units of wave-number equal to  $N$  say, then  $d\nu/dl$  must be constant and equal to  $N$ .

For this to be so  $(u-f-s \sin \phi)$  must always be proportional to  $\{\lambda_0(s+s_0)+c\}$ , i.e.,  $(u-f) = -\sin \phi (c+\lambda_0 s_0)/\lambda_0$  for all values of  $s$ .

Then 
$$\left\{ \frac{u-f-s \sin \phi}{\lambda_0(s+s_0)+c} \right\}^2 = \frac{\sin^2 \phi}{\lambda_0^2} \quad \dots \quad (7)$$

$$k^2 = \cos^2 \phi + \frac{v^2}{u^2} \sin^2 \phi = \cos^2 \phi + \frac{f^2}{(u-f)^2} \sin^2 \phi \quad \text{by (1)}$$

$$k^2(u-f)^2 = f^2 \sin^2 \phi + \cos^2 \phi \cdot \frac{\sin^2 \phi}{\lambda_0^2} (c+\lambda_0 s_0)^2 \quad \dots \quad (8)$$

By (7) & (8) we get from (6):

$$N^2 = \left( \frac{d\nu}{dl} \right)^2 = \frac{10^{16} c^2 \sin^2 \phi}{f^2 \cdot \lambda_0^2 \{ f^2 \lambda_0^2 + (c + \lambda_0 s_0)^2 \} \cos^2 \phi} \quad \dots \dots \dots (9)$$

$$\therefore N^2 f^2 \lambda_0^2 \{ f^2 \lambda_0^2 + (c + \lambda_0 s_0)^2 \} = \sin^2 \phi \{ 10^{16} c^2 + N^2 f^2 \lambda_0^2 (c + \lambda_0 s_0)^2 \}$$

$$\therefore \sin^2 \phi = \frac{N^2 f^2 \lambda_0^2 \{ f^2 \lambda_0^2 + (c + \lambda_0 s_0)^2 \}}{10^{16} c^2 + N^2 f^2 \lambda_0^2 (c + \lambda_0 s_0)^2} \quad \dots \dots \dots (10)$$

all the constants involved on the right-hand side being known,  $\sin \phi$  and therefore  $\phi$  can be evaluated.

$\psi$  is given by  $\tan \psi = (v/u)$ ,  $\tan \phi = \{f/(u-f)\}$ .  $\tan \phi$  by (1) and (3) and substituting for  $(u-f)$  we have

$$\tan \psi = - \frac{f \lambda_0 \tan \phi}{\sin \phi (c + \lambda_0 s_0)} \quad \dots \dots \dots (11)$$

$$u \text{ is given by } u-f = - \frac{\sin \phi}{\lambda_0} (c + \lambda_0 s_0) \quad \dots \dots \dots (12)$$

As  $(u-f)$  must be positive we should only take the negative values of  $\sin$  from (10).

$$v \text{ is given by } v = \frac{fu}{u-f} = - \frac{fu \lambda_0}{\sin \phi (c + \lambda_0 s_0)} \quad \dots \dots \dots (12a)$$

If we have a grating spectrum on the plate PS for which the wavelength is given by the linear formula  $\lambda = \lambda_0 + cs$ , we have  $d\lambda/ds = c$ ,

$$\frac{d\nu}{dl} = \frac{d\nu}{d\lambda} \cdot \frac{d\lambda}{ds} \cdot \frac{ds}{dl} = - \frac{10^8}{\lambda^2} \cdot c \cdot \frac{(u-f-s \sin \phi)^2}{fk(u-f)}$$

$$\text{substituting for } \lambda^2, \frac{d\nu}{dl} = - \frac{10^8 c}{fk(u-f)} \cdot \frac{(u-f-s \sin \phi)^2}{(\lambda_0 + cs)^2} \quad \dots \dots \dots (13)$$

for this to be constant equal to M say,  $(u-f-s \sin \phi)$  should always be proportional to  $(\lambda_0 + cs)$ , i.e., for all values of  $s$ ,  $(u-f) = (-\lambda_0 \sin \phi)/c$  and then,

$$\frac{(u-f-s \sin \phi)^2}{(\lambda_0 + cs)^2} = \frac{\sin^2 \phi}{c^2} \quad \dots \dots \dots (14)$$

$$k^2 (u-f)^2 = (u-f)^2 \left\{ \cos^2 \phi + f^2 \frac{\sin^2 \phi}{(u-f)^2} \right\} = \sin^2 \phi \left\{ f^2 + \frac{\lambda_0^2}{c^2} \cdot \cos^2 \phi \right\} \dots \dots (15)$$

With the help of (14) and (15) we get from (13)

$$M^2 = \left( \frac{d\nu}{dl} \right)^2 = \frac{10^{16} c^2}{f^2} \cdot \frac{\sin^2 \phi}{c^2} \cdot \frac{1}{f^2 c^2 + \lambda_0^2 \cos^2 \phi} \quad \dots \dots \dots (16)$$

$$\text{giving } \sin^2 \phi = \frac{M^2 f^2 (\lambda_0^2 + f^2 c^2)}{10^{16} + N^2 f^2 \lambda_0^2} \dots \dots \dots (17)$$

$$\psi \text{ is given by } \tan \psi = \frac{f}{u-f} \tan \phi = -\frac{fc \tan \phi}{\lambda_0 \sin \phi} = -\frac{fc}{\lambda_0 \cos \phi} \dots \dots \dots (18)$$

$$u \text{ is given by } (u-f) = \lambda_0 \sin \phi / c \dots \dots \dots (19)$$

$$\text{and } v = fu / (u-f) = -fcu / \lambda_0 \sin \phi \dots \dots \dots (20)$$

As in prismatic spectra the negative value of  $\sin \phi$  is to be taken. As  $s$  is the distance measured from the centre of the plate,  $\lambda_0$  represents the wavelength at the centre.

Taking a particular example for the prismatic spectra, the interpolation formula was given by  $\lambda = 1025.78 + 811922.8 / (s + 588.005)$ ,  $s$  being measured from the centre of the plate, increasing in direction of decreasing wave-lengths and expressed in millimetres.  $N$  was taken equal to 10 units of wave-number per 1 mm.; the focal length  $f = 7.8$  ins. = 198.12 mms.

$$\lambda_0 = 1025.78, \text{ and } c = 811922.8.$$

Substituting in (10), we get after some calculation,

$$\phi = 2^\circ 3', \psi = 8^\circ 11', u = 247.45 \text{ mms.}, \text{ and } v = 993.80 \text{ mms.}$$

Wavelengths in air were used in the interpolation formula in the above example. For greater accuracy wave-lengths corrected to vacuum should be used.

It will be observed that the formulæ thus deduced for the conversion of prismatic and grating spectra to the scale of normal frequencies would be exact if the dispersions were accurately represented by the Cornu-Hartmann and linear formulæ respectively. In practice these are only close approximations and in neither case can exact reproductions on the normal frequency scale be made. The results obtainable, however, are of sufficient accuracy to be of service in the preliminary examination of spectra for the detection of recurring frequency differences.

For very complex spectra the method is not useful, for the large number of lines, and the comparatively wide limits which have to be assigned to the accuracy of the constant differences searched for, make the number of apparently equal differences too large.

However, for spectra with moderate number of lines, the method is to be recommended, especially, when the differences to be searched for are not well known.

In order to test the results experimentally, an apparatus not much different from that of Fowler and Eagle was used. The frame ordinarily used for carrying the negative in the enlarging apparatus was supplemented by one which could



be rotated about a horizontal axis at the centre. The plate was mounted vertically. To the side, at the lower end of the original frame, was screwed a millimetre scale while the rotating frame was provided with a pointer. Thus the  $\angle \phi$  could be easily set. In front of the usual copying board of the enlarging apparatus, at its top, was hinged a board which could thus be made to rotate round a horizontal axis. A scale was attached to the usual copying board and the rotating board carried a pointer allowing for the adjustment of  $\angle \psi$ . The distance  $u+v$  was adjusted by moving the enlarging lens.

In conclusion it is a pleasure to express my thanks to Prof. A. Fowler in whose Laboratory at the Imperial College of Science and Technology, this work was carried out.

#### *Reference*

- <sup>1</sup> Fowler and Beals, *Astro. Journ.*

# ABSORPTION SPECTRA OF SOME HALOGEN-DERIVATIVES OF METHANE

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## Introduction

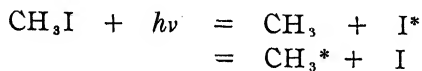
Up to the present time not much work has been done on the absorption spectra of polyatomic molecules, though the need for such investigations has been keenly felt, as they promise to furnish supplementary grounds on which the structural models of these molecules may be built. In such works difficulty is encountered both in respect of experimental technique, as well as in the interpretation of results. In case of organic substances the main difficulty consists in maintaining a suitable range of vapour pressure of the absorbing gas at ordinary temperatures (*e.g.*, for  $\text{CHCl}_3$ ,  $\text{CHBr}_3$ ,  $\text{CHI}_3$ , etc. . .), and sometimes in obtaining the substance in a state of high degree of purity (*e.g.*, for  $\text{CH}_3\text{Cl}$ ,  $\text{C}_2\text{H}_5\text{Cl}$ , etc.) which is essential for getting any correct result. No less difficulty is felt in experimenting with polyatomic inorganic compounds; thus, for example, the commonest among them, the oxides of the alkali metals have to be heated in a very high temperature-furnace for getting appreciable vapour pressure. Besides, many of these substances, both organic and inorganic (*e.g.*, bromoform, nitrous oxide, etc.), attack mercury, india-rubber, and sealing wax, so that it becomes a matter of considerable difficulty to maintain and measure the pressure of the absorbing gas column. Nevertheless important works on the absorption spectra of many alkyl halides have been done by Herzberg<sup>1</sup> and Schiebe, Mecke<sup>2</sup>, Iredale<sup>3</sup> and Mills and others, and those of saturated halides of multivalent elements have been studied by Saha<sup>4</sup>, Datta, Deb<sup>5</sup>, and others in this laboratory.

According to Franck and Kuhn's well-known hypothesis, the limit of continuous absorption towards the long wavelength side of the spectrum corresponds to the beginning of photo-dissociation of the molecule. On this basis it is possible to

determine the strength of the carbon-halogen bond from the study of the beginning of continuous absorption of saturated alkyl-halides and some other organic compounds of carbon, hydrogen, and halogens. This has necessarily added a special importance to the study of the absorption spectra of polyatomic substances.

While most of the early observers have found that the absorption spectra of the alkyl-halides consist entirely of continuous absorption beginning from a long wavelength limit and extending towards the short wavelength side within a region  $\lambda$  3000 to  $\lambda$  2000, band-absorptions in the case of  $\text{CH}_3\text{Cl}$  have been found by Herzberg and Scheibe, and more recently in the case of  $\text{CCl}_4$ ,  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ , ... by A. Henrici<sup>6</sup> in the region  $\lambda$  2000 to  $\lambda$  1400. Saha and Datta, in their study of the absorption spectra of a number of tetra-halides including  $\text{CCl}_4$ , have tried to make the generalisation that the energy of photo-chemical dissociation of such compounds is one-fourth the total atomic heat of formation; or, in other words, in  $\text{CCl}_4$  the total heat of formation is equally distributed among the four halogen-bonds of carbon. Iredale and Mills from the photometric study of the absorption limit of  $\text{CH}_3\text{I}$ ,  $\text{C}_2\text{H}_5\text{I}$ , etc., have attempted to emphasise that the C atom in such alkyl-halides exists in  $2s2p^3^5S$  state, and not in the  $2s^22p^2^3P$  state as assumed by Herzberg and Scheibe. They have tried to show further that their fresh determinations of absorption limits of these substances are consistent with this view. Regarding most of these works it may be remarked, however, that the experimental methods employed in the determination of the long-wavelength limit, which is rather ill-defined, are not above criticism. On the other hand, from the isolated data that can be procured from these works on some of the halogen derivatives of methane (*e.g.*,  $\text{CCl}_4$ ,  $\text{CH}_3\text{Cl}$ , etc.) it is not possible to arrive at any definite conclusion regarding the gradual formation of these derivatives by the replacement of H atoms of methane successively by one, two, or more Cl-atoms—a subject which has acquired considerable importance from the study of the dielectric moments<sup>7</sup> of these compounds. The purpose of the present paper has been to provide a systematic study of the di-, tri- and tetra-halogen derivatives ( $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , and  $\text{CCl}_4$ ) of methane in relation to the value of the C-Cl bond energy, as calculated from the measurement of the beginning of their continuous absorption.

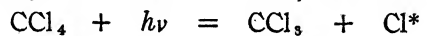
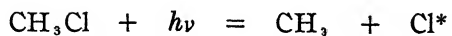
The nature of photo-chemical dissociation taking place in these cases is a matter of some uncertainty. Herzberg and Scheibe, in their investigations on the continuous and discontinuous light absorption by methyl halides, have assumed the process of dissociation as—



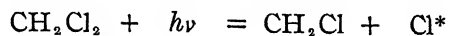
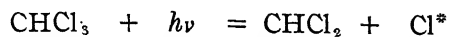
where  $\text{M}^*$  denotes an excited state of M, *i.e.*, the effect of light absorption is the dissociation of the compound into a normal and an excited radical. Iredale and Mills<sup>3</sup> in their papers on  $\text{CH}_3\text{I}$ ,  $\text{C}_2\text{H}_5\text{I}$  ... definitely assert that the products of

dissociation for such compounds are one *neutral alkyl radical and an excited halogen atom*.

Assuming this to be true the dissociation of  $\text{CH}_3\text{Cl}$  and  $\text{CCl}_4$  is supposed to consist of—



*i.e.*, in each case the effect of light absorption is the dissociation of a C-Cl bond, and the energy  $h\nu$  required for this purpose marks the beginning of the continuous absorption. Extending the same principle to the intermediate compounds of the series we may write—



The potential energy curves for the states of the molecules before and after dissociation are represented in Fig. 1. In the normal state A the molecule is supposed to consist of a central C atom electrically bound to four other (H or Cl)

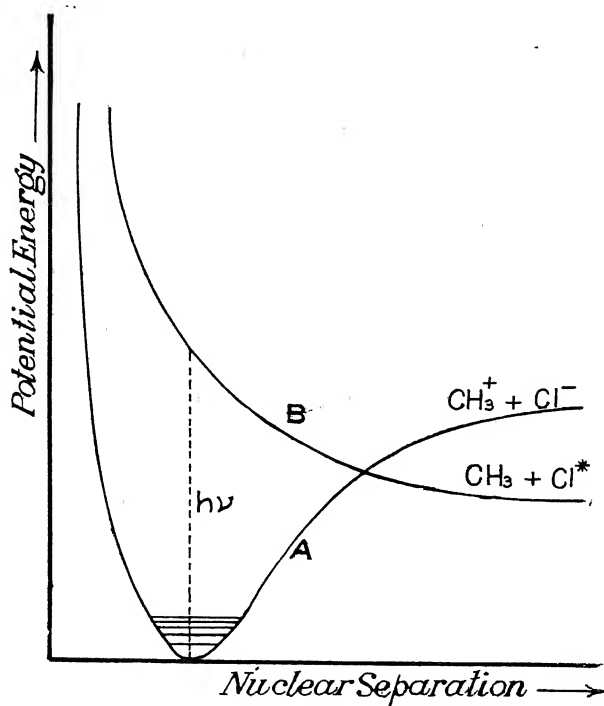


Fig. 1

atoms, which have each taken up an extra electron from the atom, which has thus lost four of its outer electrons. The second state B is brought about in each case by the transference of an electron from the  $\bar{\text{Cl}}$ -ion to the  $\text{C}^+$ -ion by light

absorption. Since the same amount of energy  $h\nu$  is required for this electronic transition in the molecule in each case, the beginning of continuous absorption for all members of the series should be precisely the same. The observations embodied in the present paper show a certain amount of disagreement from this conclusion.

### The Experimental Procedure

The method employed for the study of the beginning of the continuous absorption of  $\text{CCl}_4$ ,  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$  is that previously used by Datta<sup>9</sup> in this laboratory. The substance under investigation, usually a liquid, is contained in a bulb  $B$  (Fig. 2), and its vapour is enclosed at room temperature in a pyrex glass tube about one metre long, and closed at both ends by quartz plates  $P, P$ . Light was allowed to pass through the tube from a continuous source  $S$  (a hydrogen discharge tube)

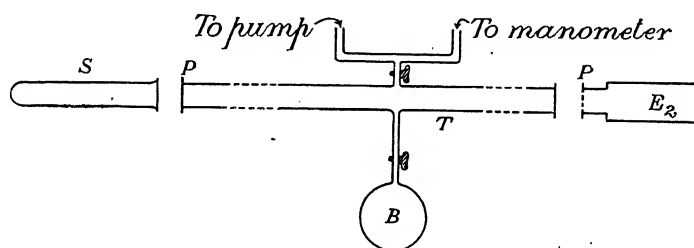


Fig. 2

placed co-axially with the absorption tube, and the spectrum of the transmitted light was photographed in the usual way by an  $E_2$ -quartz spectrograph. The pressure inside the absorption tube could be adjusted by means of a vacuum pump attached to the tube, and read directly by a manometer. As almost all the compounds examined attacked india-rubber and sealing-wax, difficulty was experienced in connecting the bulb and sealing the quartz plates to tube ends. The difficulty was overcome by making the side-connections entirely of glass and using mainly plaster of Paris as the substance for sealing. A copper arc was used as a source of comparison spectrum. Different photographs were obtained for the same substance with different pressures of the absorbing gas. Continuous spectrum was obtained in each case, the beginning of which was found visually to shift with pressure.

### The Determination of the Limit

The exact determination of the beginning of continuous absorption from these photographs is a matter of considerable difficulty, as the limit is not at all well-defined, and moreover, because the visible limit seems to change with the pressure of the gas and the length of the absorbing column. In fact, Franck and Kuhn in a private note addressed to Prof. Saha have pointed out that from theoretical considerations the limit of continuous absorption ought to extend over

a short region of wavelength rather than corresponding to a sharp limit. For the electronic transition which is associated with the photo-dissociation of the compound may take place not only from the ground state of the molecule, but also from a number of closely lying vibrational states of excitation (Fig. 1).

The visual method sometimes employed is obviously very inaccurate, as the decrease in intensity actually begins much earlier (towards the longer wavelength side) than can be detected by the eye. Iredale and Mills have used a photometric method. From the micro-photometric record of the absorption spectrum the beginning of continuous absorption is traced, and the corresponding wavelength is known with the help of the comparison spectrum micro-photographed on the same plate. The accuracy of this method depends entirely on the sensitiveness of the micro-photometric record. It has been observed, however, that the recording instrument does not respond well to small changes of density of the photographic image, which is essential for accurate determination of the limit.

The method adopted in the present work is that due to Herzberg and Scheibe, later on employed by Datta<sup>2</sup>, and one which appears to be less objectionable. Corresponding to a particular wavelength in the comparison spectrum micro-

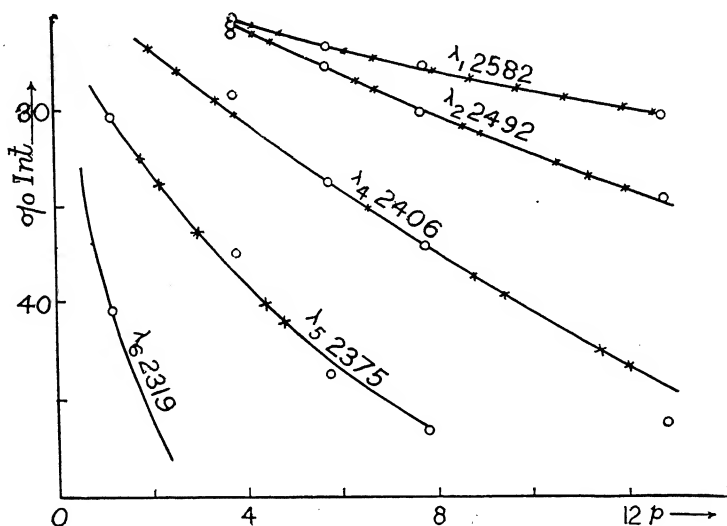


Fig. 3

photometric records are obtained for the regions in the absorption spectra of different pressures. Taking the intensity of the continuous spectrum as 100, the intensities corresponding to other pressures are calculated. A curve is then drawn with the pressure along the X-axis and intensity along the Y-axis, which becomes exponential in nature, the intensity falling off according to a relation  $I = I_0 e^{-\alpha p}$  where  $\alpha$  is the coefficient of extinction;  $\alpha$  is calculated for different wavelengths of the spectrum  $\lambda_1, \lambda_2, \lambda_3, \dots$ . A curve is then plotted with

wavelength as abscissa and the extinction coefficient as ordinates. On extrapolating this curve the wavelength corresponding to zero extinction coefficient is obtained, which must be the beginning of continuous absorption. The two sets of curves for  $\text{CCl}_4$  and  $\text{CH}_2\text{Cl}_2$  are shown in Figs. 3, 4, 5, 6.

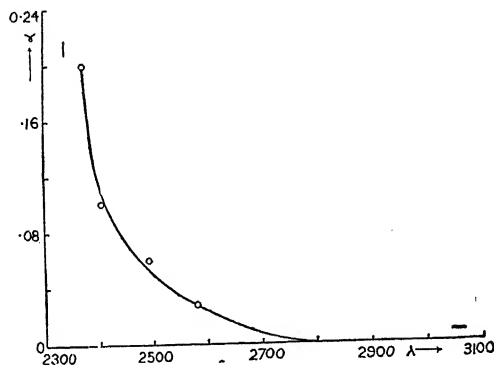


Fig. 4

One great advantage of this method over others is that it eliminates the uncertainty due to the arbitrariness of the gas pressure and length of the absorbing column.

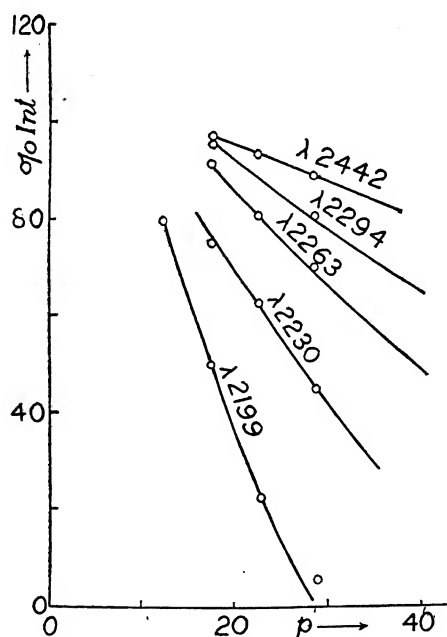


Fig. 5

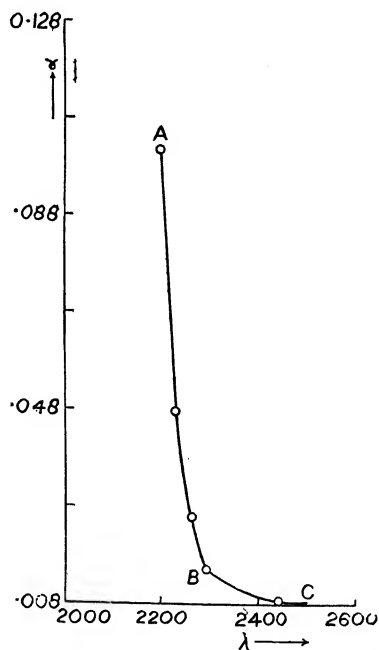


Fig. 6

The absorption limits obtained by this method are shown in the following table.

TABLE 1

| Substance                       | $\lambda$ in Å. U. limit | $Q_m = h\nu$ in k cal. for C—Cl bond. | $Q_m = h\nu$ in k cal. for C—H bond. |
|---------------------------------|--------------------------|---------------------------------------|--------------------------------------|
| C Cl <sub>4</sub>               | 2800                     | 102                                   | —                                    |
| CH Cl <sub>3</sub>              | 2660                     | 107.5                                 | ?                                    |
| CH <sub>2</sub> Cl <sub>2</sub> | 2500                     | 114.4                                 | 124                                  |

The third column represents the molecular energy  $Q_m$  corresponding to the beginning of absorption  $\lambda$  (limit) expressed in k cal. This is calculated according to the relation—

$$Q_m = \frac{N h \nu_m}{J}$$

where  $N$  = Avogadro number and  $\nu_m$  = the limiting frequency corresponding to  $\lambda$  (limit). This evidently denotes the energy of the bond in each case.

### Calculations from Thermo-chemical Data

The energy of the C—Cl bond can be calculated for each of the above compounds from its known heat of combustion and some other thermo-chemical data. Take the case of C Cl<sub>4</sub>. Assuming the C atom in the formation of this molecule to exist in <sup>5</sup>S-state, heat of sublimation of C from solid to <sup>3</sup>P-state equal to 161 k cal. and the energy difference C(<sup>5</sup>S) — C(<sup>3</sup>P) = 119 k cal\*, we get—

$$[C]_{\text{solid}} = C(^3P) - 161 \text{ k cal.}$$

$$C(^3P) = C(^5S) - 119 \text{ k cal.}$$

$$[C] = C(^5S) - 280 \text{ k cal.}$$

i.e., the total heat of sublimation of C = 280 k cal. Now heat of formation of CO<sub>2</sub> = 94 k cal.

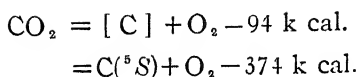
\* The heat of sublimation of C (in the <sup>3</sup>P-state) is rather uncertain. The usually accepted value due to Kuhn and Guckel (*Zeits f. Physik*, 27, 305, 1924) is 139 kcal. while in a recent note published in the *Phys. Rev.* (41, 1932) a value ranging between 161 to 176 k cal has been given. Here we have taken the lower limit 161 k cal.

The energy of excitation C(<sup>5</sup>S) — C(<sup>3</sup>P) is also equally uncertain. Heitler and Herzberg<sup>10</sup> from the considerations of the quantum mechanical theory of homopolar bonds estimated this energy to be 1.6 volts which is about 37 kcal. Iredale and Mills on the other hand assume that the C atom exists in CO<sub>2</sub> in the quintet state and in CO in the triplet state, and that the energy of binding of C in O=C=O is double that in C=O. Taking the heat of sublimation of C to be 139 k cal, they calculated the energy of excitation from the triplet to the quintet state to be 97 k cal, i.e. about 4 volts. It is to be seen that the two values are widely divergent nor any of the two methods of calculation is based on solid grounds, though both of them admit that the triplet state is deeper than the quintet state. In this paper Iredale and Mills' method has been followed and using the heat of sublimation as 161 k cal the energy of excitation re-calculated is 119 k cal which is about 5 volts.

Heat of formation of H<sub>2</sub>O refers to the vapour state. Other data have been taken from Landolt and Börnstein's tables.

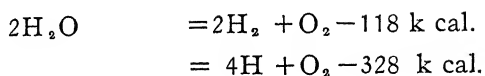


Thus



Heat of formation of  $\text{H}_2\text{O}$  = 59 k cal.

Heat of dissociation of  $\text{H}_2$  = 105 k cal.

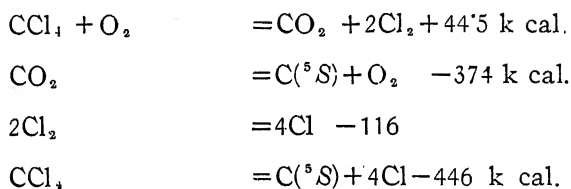


Energy of the C-H bond = 123 k cal.

Heat of combustion of  $\text{CCl}_4$  = 44.5 k cal.

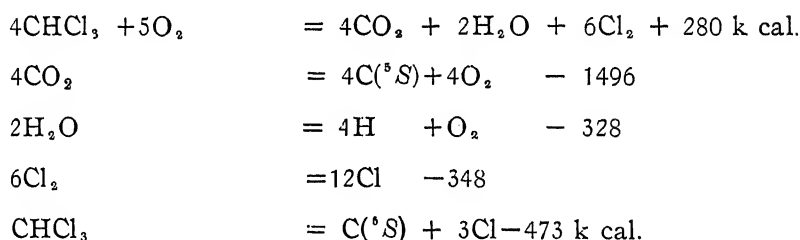
Heat of dissociation of  $\text{Cl}_2$  = 58 k cal.

Thus



Assuming this energy to be equally distributed among the four carbon halogen bonds, the energy of the C-Cl bond = 111.5 k cal.

Similarly using the heat of combustion of  $\text{CHCl}_3$  = 70 k cal; we get



Subtracting C-H bond energy = 123 k cal., C-Cl bond energy comes out to be 116.5 k cal.

In the same way for  $\text{CH}_2\text{Cl}_2$ , the energy of the C-Cl bond is calculated to be 121.5 k cal. using the heat of combustion for this compound as 106.8 k cal.

The quantitative values calculated above are likely to be questioned when one considers the fundamental assumption made regarding the state of the carbon atom. The ground state of C atom according to its electronic structure is  $2s^2 2p^2$ . But it has been supposed that in the above compounds C exists

in  $^5S$ -state. The origin of such an assumption is a theoretical conclusion reached by Heitler and London on the chemical valency of elements, *viz.*, the valency of an element in molecular formation is numerically equal to the multiplicity of the ground state of the element diminished by one. Since in  $\text{CH}_4$  and its substituted halogen-derivatives C is regarded as tetravalent, the multiplicity of the ground state is supposed to be five. From spectroscopic point of view the  $^5S$ -state of the C atom may arise if the configurations of its 6 electrons be  $1s^2 2s^2 2p^3$ , instead of  $1s^2 2s^2 2p^2$  as in the normal atom. The possibility for the existence of such a configuration of C atom in these compounds is doubtful and requires confirmation from other sources.

### Discussion of Results

The experimental results given in (table 1) definitely show that there is a regular shift of the beginning of absorption towards longer wavelength as we pass from one to the other compound of the series  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ ,  $\text{CCl}_4$  by an amount very nearly equal to 150 Å.U. This is equivalent to the fact that assuming the strength of the C—H bond to remain constant throughout, the strength of the C—Cl bond diminishes as we gradually replace the H atoms of  $\text{CH}_4$  by more and more Cl atoms. An inspection of the results calculated from thermochemical data exhibits a similar variation of the strength of the C—Cl bond. It may be objected, however, that the latter calculations have been based on the assumption that in a compound like  $\text{CH}_n\text{Cl}_{4-n}$  the C atom exists in  $^5S$ -state. To this objection it may be answered that even though there is such uncertainty regarding the state of the C atom in these compounds, and consequently the heat of sublimation of C, this does not affect very much our conclusion regarding the *differences of bond energies*.

An examination of curve ABC (Fig. 7) for  $\text{CH}_2\text{Cl}_2$  reveals a discontinuity at the point B. The discontinuity of the curve at this region seems to have special significance. The curve ABC may be looked upon as being composed of two curves  $A_1BC$  and  $A_2B'$  shown by dotted lines, superposed on each other. The curve is thus composite; and the best way to explain this is to assume that here we have to deal with two photochemical processes, *viz.* (A) the photochemical disruption of the C—Cl bond beginning at  $\lambda 2500$  and represented by curve (1), and (B) photochemical disruption of the C—H bond beginning at  $\lambda 2290$ , and represented by curve (2). According to this interpretation, the value of the C—H bond is 124 k cal. This result is in fair agreement with the commonly accepted value of C—H bond-energy as 123 k cal. It is remarkable that the absorption curve for  $\text{CCl}_4$  does not represent any such discontinuity, there being only one type of energy bond, *viz.*, C—Cl present in the molecule.

The absorption curve for  $\text{CHCl}_3$  should also show similar discontinuity. Unfortunately the experimental curve obtained is not very conclusive. The

experiment, specially the microphotometric records are being repeated to decide this point.

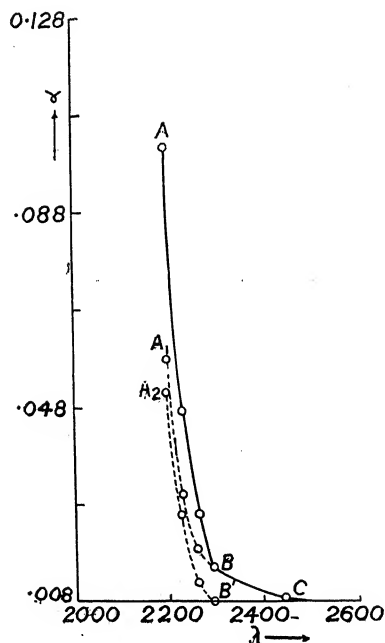


Fig. 7

The reason for the observed variation of C—Cl bond energy is not very clearly understood. It appears reasonable to think that the interaction between Cl atoms, which increases with the increase of the number of Cl atoms, in the molecule, is responsible for the weakening of the bond strength, by setting up some sort of constraint of the carbonhalogen bonds.

A molecule of  $\text{CH}_4$  is represented by symmetrical tetrahedral structure with the C atom at the centre, and the four H atoms at the four apices of a regular tetrahedron (Fig. 8). Such a structure is supported by (i) the study of the X-ray diffraction pattern of the crystal structure of a certain tetra-substituted derivatives of methane of the form  $\text{C}(\alpha)_4$ , by Nitta,<sup>11</sup> Schleede<sup>12</sup> and others, and (ii) by the absence of electric moment in  $\text{CH}_4$  and a few of its tetra-substituted derivatives. We may then suppose that in  $\text{CH}_4$  molecule four equal forces acting from the central carbon atom towards the four H atoms are producing an equilibrium. Let us now think that the two of the H atoms are replaced by two Cl atoms, as in  $\text{CH}_2\text{Cl}_2$ . For such a molecule the structural model will evidently be a distorted tetrahedron, the distortion being brought about mainly by two causes :—(1) the forces acting from the C atom towards the apices being unequal

the position of the carbon atom will be shifted from the centre of the tetrahedron ; (2) the radius of the sphere of collision of a Cl atom is much larger than that of a H atom. Assuming two H atoms in  $\text{CH}_4$  to be separated by a distance not much

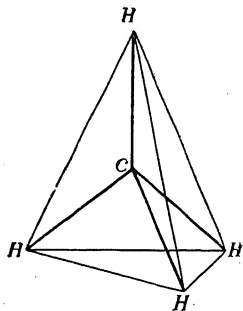


Fig. 8

greater than the diameter of the sphere of collision of an H atom, as soon as the two H atoms are replaced by two Cl atoms, the angle between the two C—Cl bonds must widen so that the two Cl atoms may remain uncompressed. So gradually by increasing the number of Cl atoms in the molecule, the amount of distortion relative to the symmetrical structure will more and more increase, as the conditions in both the factors (1) and (2) will be changed. Therefore, compared to one compound of the series, say  $\text{CH}_2\text{Cl}_2$ , the constraints in the bonds of the next compound  $\text{CHCl}_3$  will have a change which will alter the strength of the carbonhalogen bond.

The variation of the dipolemoment<sup>13</sup> of compounds of the series  $\text{CH}_4$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ ,  $\text{CCl}_4$  from one to the other member is well known. The amount of variation cannot be explained on the simple basis of the substitution of a Cl atom for a H atom in the symmetrical tetrahedral model. The distortion of the tetrahedron due to the two causes must be taken into account. The effect due to the cause (2) is very uncertain, and it seems, no proper allowance has been made for it in theoretical calculations. We may suppose that this effect is equivalent to an alteration of the C—Cl bond strength as obtained from the study of their continuous absorption spectrum. Thus, if proper allowance is made for the variation of the C—Cl bond energy in the successive compounds, the effect due to the second cause becomes practically incorporated in that due to the first. The latter can be calculated from the geometry of the regular tetrahedron and the statical conditions of equilibrium of forces. So a fresh calculation of the electric moments of these compounds may be attempted on this basis. It must be confessed that the accuracy of the absorption data is not at present very great. But still an approximate result can at any rate be expected.

In conclusion I wish to express my sincere thanks to Prof. M. N. Saha, F.R.S. for his kind guidance and valuable suggestions throughout the progress of the work.

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- <sup>8</sup> A. K. Datta, Absorption Spectra of  $\text{SO}_2$ , and Heat of Dissociation of Oxygen: *Proc. Roy. Soc. A* 137, 366, 1932.
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# ON THE ABSORPTION SPECTRA OF THE OXIDES OF ZINC AND CADMIUM

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Communicated by Prof. M. N. Saha.

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## Introduction

The following experiments were undertaken with a view to extending Franck's theory of action of light on saturated chemical compounds. The group chosen in these series consist of oxides and sulphides of a simple form. Experiments on  $\text{SO}_2$ ,  $\text{N}_2\text{O}_3$ ,  $\text{TeO}_3$ , and  $\text{MoO}_3$  by A. K. Datta and the present author<sup>1</sup> have already been reported. In the present communication the results of experiments with saturated monoxides, *viz.*,  $\text{ZnO}$  and  $\text{CdO}$  are reported.  $\text{HgO}$  was also tried, but this substance readily decomposes before any appreciable vapour is available, and no positive results were obtained.

## Experiment

Since the oxides of Zinc and Cadmium begin to vaporise at rather high temperatures (from about  $1000^\circ\text{C}$  and  $800^\circ\text{C}$  respectively), the vacuum graphite furnace of this laboratory was utilised. The oxides were introduced in silica tubes 20 cms. long into the furnace. The source of continuous spectrum was a Hydrogen tube run by a 2 KW. transformer, and the photographs were taken on an  $\text{E}_3$  quartz spectrograph. Exposures of 2 to 4 minutes were sufficient. The copper arc was used for comparison.

## Results

Two sets of experiments were undertaken, one with varying temperatures in vacuum and the other under similar conditions with air inside the absorption chamber. Air served only to prevent the distillation of the vapours, as well as to introduce a small quantity of Oxygen into the absorption chamber. Pure Oxygen under atmospheric pressure could be used, but the presence of the large quantity of Oxygen causes the graphite tubes to burn away in no time at the high temperatures used, making observation almost impossible.

**CdO.—Experiments in vacuum.**—The vacuum was of the order of 1 to 2 mms. and the pump was kept running continuously throughout. Light was found to be cut off in the ultra-violet from a long wave limit about 2150 Å. The continuous absorption was rather extended on account of the low pressure of CdO vapour. Higher temperatures revealed some bands in some of the plates. The following is a list of some of them.

|      |      |
|------|------|
| 2107 | 2067 |
| 2099 | 2047 |
| 2086 | 2026 |
| 2076 |      |

These bands could easily be identified with those of  $\text{CO}^2$

Now at high temperature of the order of 1200°C CdO decomposes into Cd and  $\text{O}_2$  with the result that the resonance line 2288 ( $1s-2p$ ) was obtained in absorption. But at the same time the graphite of the furnace tube vaporises and forms with the liberated Oxygen, CO and  $\text{CO}_2$ .

**CdO.—Experiments in Air.**—When the furnace is filled with air and pump is not run we can expect thermodynamical equilibrium to hold good. We have then

$$\frac{P_{\text{Cd}}}{P_{\text{CdO}}} = \sqrt{\frac{K}{P_{\text{O}_2}}} = \text{constant.}$$

Since the value of K rapidly increases with T, and  $P_{\text{O}_2}$  is almost constant and  $P_{\text{CdO}}$  is given by the saturated vapour pressure of CdO,  $P_{\text{Cd}}$  would increase very rapidly with temperature.

This circumstance explains the results. The absorption of the resonance line  $^1\text{S}-^1\text{P}$  becomes very broad and the intercombination line  $\lambda$  3267 ( $^1\text{S}-^3\text{P}$ ) now becomes discernible showing that we have much more Cd-vapour now in the absorption vessel. It is also clear from the appearance of  $\text{Cd}_2$  bands which were first discussed by Winans.<sup>3</sup> These are highly developed as T increases, and their breadth reaches the enormous extent of 160 Å units nearly. Besides the 2288 band the 2212 band recorded by Winans was obtained and also a line at 2136 which is easily identified with the resonance line of Zinc probably occurring as an impurity in the CdO.

The continuous absorption by the Oxide was very prominent under these conditions (high temperatures, tube filled with air) as CdO-gas has now chances of reaching the equilibrium value. The cut off is found to begin from 2100 Å units.

**ZnO.**—The behaviour of Zinc Oxide is similar to that of Cadmium Oxide. In vacuum the CO-bands were obtained, and the absorption by the Oxide was not very well defined. In the presence of air, the asymmetric broadening of the resonance line 2136 of Zinc due to the formation of  $\text{Zn}_2$  molecule was present along with band absorptions of  $\text{Zn}_2$ -molecule. The absorption by the Oxide was better defined

and obtained at  $2000\text{\AA}$ . The intercombination Zinc resonance line  $^1S-^3P$  was not obtained in absorption. This is probably due to the comparative faintness of this line compared with that of Cadmium.

It might be mentioned here that in the absorption of both ZnO and CdO in air at very high temperatures some of the long wave members CO bands were obtained.

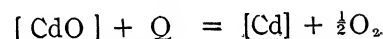
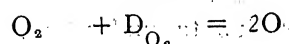
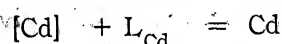
### Calculations

From theoretical considerations



$$\text{and } R = N\hbar\nu_1/J$$

where R can be determined with the aid of the following relations



$$\therefore R = Q + \frac{1}{2}D_{\text{O}_2} + (L_{\text{Cd}} - L_{\text{CdO}})$$

in which

$Q$  = Heat of formation of  $[\text{CdO}]$  from  $[\text{Cd}]$  and  $\text{O}_2$

$L_{\text{Cd}}$  = Latent heat of sublimation of Cd

$L_{\text{CdO}}$  = Latent heat of sublimation of CdO

$D_{\text{O}_2}$  = Heat of dissociation of  $\text{O}_2$

Out of these  $Q$  and  $L_{\text{Cd}}$  can be found in Landolt and Bornstein's tables.  $D_{\text{O}_2}$  has been estimated by Datta<sup>1</sup> to be 128 k cal and by Herzberg to be 117 k cal. But  $L_{\text{CdO}}$  is unknown, and it has been roughly estimated with the help of Trouton's rule as follows:—

$$\frac{L_{\text{CdO}}}{T} = 23 \text{ where } T \text{ is the boiling point at the absolute temperature.}$$

$$\therefore L_{\text{CdO}} = 23 (1000 + 273) \\ = 292 \text{ k cal nearly.}$$

$$\therefore R = 63 + 64 + (26 - 292) \\ = 124 \text{ k cal nearly.}$$



Experimentally the limit of absorption comes out to be  $2100\text{\AA}$ , which is equivalent to 135 k cal.

**ZnO: -**

$$\begin{aligned} R &= Q + \frac{1}{2} D_{O_2} + (L_{Zn} - L_{ZnO}) \\ &= 85.4 + 64 + (31.3 - 47) \\ &= 134 \text{ k cal nearly.} \end{aligned}$$

Experimentally  $h\nu_{2000} = 143 \text{ k cal.}$

In both the cases the experimental value is slightly higher than the calculated value which is usually expected. In view of the fact that the estimation of the latent heats of ZnO and CdO are only rough, the agreements seem to be quite fair.

### Discussion

It is clear from the description of the behaviours of these oxides given in Mellor's Inorganic Chemistry that these substances not only give vapour at the temperatures of the order of  $1200^\circ - 1600^\circ\text{C}$ , but CdO (say) vapour is partially decomposed into Cd and  $O_2$ . This enables us to understand the experimental results given above.

As mentioned before (according to the law of mass action as worked out for me by Mr. Ram Niwas-Rai)

$$\frac{P_{Cd}^2 P_{O_2}}{P_{CdO}^2} = K$$

$$\text{or} \quad P_{Cd}/P_{CdO} = \sqrt{\frac{K}{P_{O_2}}}$$

The value of the reaction isochore cannot be calculated as most of the constants required for this purpose on the right-hand side are unknown. But it can be easily seen that when the pump is constantly run equilibrium conditions cannot be reached as there is constant flow of vapours to the cooler sides. Now Cd and CdO are deposited on the cooler parts as solids and  $O_2$  is pumped off. Hence under these conditions neither  $P_{Cd}$  nor  $P_{CdO}$  can reach very high values. This is clear from the absorption experiments. Absorption of the resonance line 2288 ( $^1S-^1P$ ) is readily obtained, but it never becomes very broad, as in the second set of experiments. As already mentioned this broadening has been attributed by Winans to the formation of  $Cd_2$  molecule which is only possible when the pressure of Cd vapour reaches above 10 mms. The order of the pressure being less than 10 mms. in the first set of experiments Winans' bands were not obtained. The appearance of the Carbon Monoxide bands has already been explained.

The absorption of the intercombination line 3267 ( $^1S-^3P$ ) is not discernible in the first set though it is prominent in the second one.

The spectrum is continuously cut off from  $2100\text{\AA}$  which we may safely ascribe to absorption by CdO vapour. In the case of ZnO this is  $2000\text{\AA}$  units.

### Conclusion

From the appearance of the continuous spectrum at the end of the spectrum it is concluded that the products of photochemical dissociation are two free atoms. In terms of potential energy curves this process is always represented by a curve of the form of  $s$  (Fig. 1). The stability of the oxides gives rise to the deep minimum of the ground state  $\alpha$ . By the transition AB due to the absorption of a quantum  $h\nu$  of light the molecule comes to B in accordance with Franck-Condon principle and simultaneously dissociation occurs. (It might be mentioned here that the maximum value of AB is given by taking A in the minimum point of the ground state, or the lowest vibration state in which the molecule exists normally. As the temperature is raised, higher vibrational states are excited so that the value of AB diminishes. For this reason in calculations,  $h\nu$  corresponding to the lowest temperatures has been used to get the maximum value of AB.

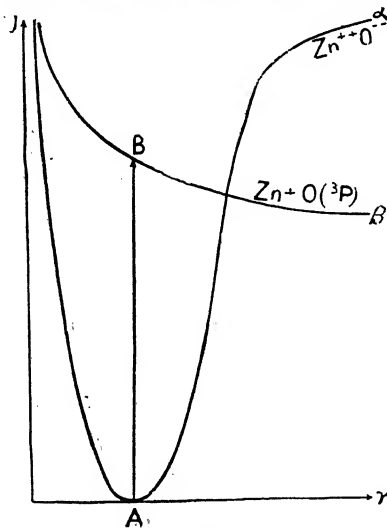


Fig. 1.

Now to account for the state  $\alpha$ , we must assume that the force of attraction is either of electrostatic origin if the compound is ionic, or it is due to "austausch" forces if it is atomic. Since the upper state is atomic the lower state is expected to be ionic. But even then there are two possibilities—

- (a) The constituents are  $\text{Zn}^{+}$  and  $\text{O}^{-}$ .
- (b) The constituents are  $\text{Zn}^{++}$  and  $\text{O}^{--}$ .

In case (a), one electron passes from  $\text{O}^{-}$  to  $\text{Zn}^{+}$ ; in case (b), both the electrons of  $\text{O}^{--}$  pass *simultaneously* due to absorption of light to the  $\text{Zn}^{++}$ -ion, giving rise to Zn and O. It will be shown that the second case is more probable, for in case (b) both  $\text{Zn}^{++}$  and  $\text{O}^{--}$  are diamagnetic, and ZnO will be diamagnetic as is actually found. If the constitution is  $\text{Zn}^{+}\cdot\text{O}^{-}$ , the compound ZnO will be paramagnetic. A consideration of the binding energies according to the Born cycle bear out the same deduction. This is shown below.

Notation :

$$I_{\text{Zn}}^{++} = \text{Sum of the ionisation potentials of Zn and Zn}^{+}.$$

## BORN-CYCLE FOR ZnO

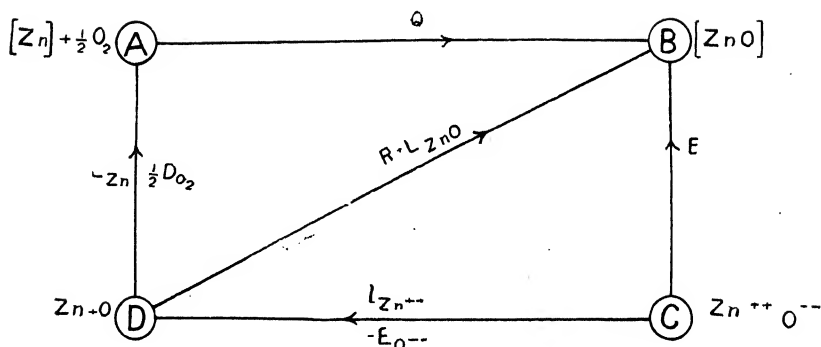


Fig. 2.

$E_{O^{--}}$  = Heat of formation of an  $O^{-}$  ion out of  $O$  and 2 electrons.

$E$  = Lattice energy, assuming that the units are  $Zn^{++}$  and  $O^{--}$ .

Other quantities have their usual meanings.

We obtain from the diagram

$$\begin{aligned}
 E &= Q + I_{Zn^{++}} + L_{Zn} + \frac{1}{2} D_{O_2} - E_{O^{--}} \\
 &= 85.4 + 628 + 31.3 + 64 - (-49) \\
 &= 857.7 \text{ k cal.}
 \end{aligned}$$

Senftleben<sup>4</sup> has given the electron affinity of  $O^{-}$  as  $-41.4$  k cal taking into account the values of  $D_{H_2}$  and  $D_{O_2}$  as 80 and 175 k cal, respectively. These values have been replaced by more recent values 95 and 128 k cal respectively in the calculations of Senftleben and the result comes out to be  $-49$  k cal for the value of  $E_{O^{--}}$ , instead of  $41.7$  k cal.

Now

$$\begin{aligned}
 R + L_{ZnO} &= E - I_{Zn^{++}} + E_{O^{--}} \\
 &= 857.7 - 628 - 49
 \end{aligned}$$

$$\begin{aligned}
 \therefore R &= (857.7 - 628 - 49) - 47 \\
 &= 133 \text{ k cal.}
 \end{aligned}$$

This value of  $R$  could also be calculated with the aid of Born and Heisenberg's formula for the crystal lattice energy. As quoted by Born and Gerlach<sup>5</sup> for ZnS

$$\begin{aligned}
 E &= K \frac{n-1}{n} \sqrt[3]{\frac{\rho}{M}} \\
 &= 2690 \cdot \frac{n-1}{n} \sqrt[3]{\frac{\rho}{M}}
 \end{aligned}$$

where  $K$  = a constant involving Madelung's coefficient,

$n$  = the repulsion exponent,

$\rho$  = the density,

$M$  = the molecular weight

Here  $n$  is given by the formula

$$n = 1 + C \times \frac{1}{X} \cdot \left( \frac{M}{\rho} \right)^{\frac{4}{3}}$$

where  $X$  the compressibility =  $77 \times 10^{-12}$  for  $\text{ZnO}$ <sup>6</sup>. Since the crystal structures of  $\text{ZnO}$  and  $\text{ZnS}$  are similar, that is of the tetrahedron type, the values of  $K$  and  $C$  will be the same.

For  $\text{ZnO}$

$$n = 1 + 8.00 \times 10^{-14} \cdot \frac{1}{X} \cdot \left( \frac{M}{\rho} \right)^{\frac{4}{3}}$$

$$= 1 + \frac{8.00 \times 10^{-14}}{77 \times 10^{-12}} \cdot \left( \frac{81.37}{5.6} \right)^{\frac{4}{3}}$$

$$\therefore = 4.64$$

$$\text{and } E = 2690 \times \frac{3.64}{4.64} \times \sqrt[3]{\frac{5.6}{81.37}}$$

$$= 865.4 \text{ k cal.}$$

From the triangle BCD of the Born cycle

$$R = 865.4 - I_{\text{Zn}^{++}} + E_{\text{O}^{--}} - L_{\text{ZnO}}$$

$$= 141.4 \text{ k cal.}$$

From experiment  $R = \frac{N h \nu_1}{J}$  comes out to be 143 k cal. The agreement seems to be quite fair.

$\text{CdO}$ .—Since Cadmium Oxide forms cubical lattices like that of  $\text{NaCl}$  or  $\text{CaO}$  we have

$$n^* = 1 + \frac{8.80 \times 10^{-14}}{75 \times 10^{-12}} \cdot \left( \frac{128.4}{8.18} \right)^{\frac{4}{3}}$$

$$= 5.61$$

$$\text{and } E = 2450 \times \frac{n-1}{n} \sqrt[3]{\frac{\rho}{M}}$$

$$= 804.6 \text{ k cal.}$$

$$R = 804.6 - I_{\text{Cd}^{++}} + E_{\text{O}^{--}} - L_{\text{CdO}}$$

$$= 128.6 \text{ k cal.}$$

Experimentally  $R = 135 \text{ k cal.}$  There is a difference of about 7 k cal between the calculated and experimental values, which is quite within limits of error.

\* The value of  $X$  not being known, a mean value of  $75 \times 10^{-12}$  from  $\text{CaO}$  and  $\text{MgO}$  and  $\text{ZnO}$  has been taken.

The foregoing shows that these oxides are ionic in compounds of the type  $\text{Zn}^{++} \text{O}^{--}$ . By the action of light both the electrons from  $\text{O}^{--}$  are simultaneously transferred to  $\text{Zn}^{++}$  with result that two normal atoms Zn and O ( $^3\text{P}$ ) are obtained, the linkage being broken.

In Fig. 1, the state  $\alpha$  represents  $\text{Zn}^{++} \text{O}^{--}$  and the state  $\beta$ , two normal and free atoms Zn and O ( $^3\text{P}$ ). There are two metastable states of Oxygen,  $^1\text{D}_2$  and  $^1\text{S}_0$ , so that a second absorption after a retransmitted patch of light is possible for  $^1\text{D}_2$  state in accordance with the process (2)



and similarly a third one for  $^1\text{S}_0$ . Thus  $h\nu_1 - h\nu_2$  from experiment should be equal to  $^1\text{P} - ^1\text{D}_2$  of oxygen, as was found to be the case by Datta and the present author for the higher Oxides. These absorption cuts are expected in the fluorite region for ZnO and CdO, and it is not possible that they can be demonstrated.

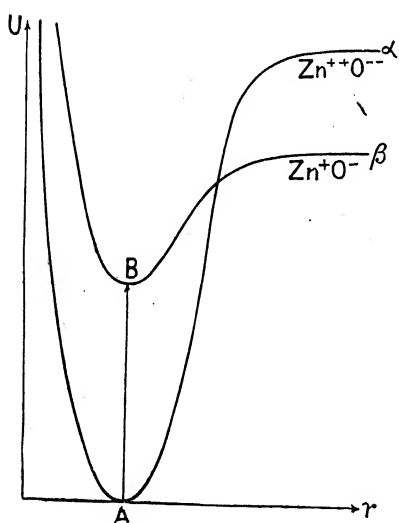
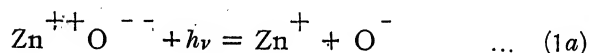


Fig. 3.

My best thanks are due to Prof. M. N Saha, D.Sc., F.R.S., for taking kind interest and rendering valuable guidance during the course of the work.

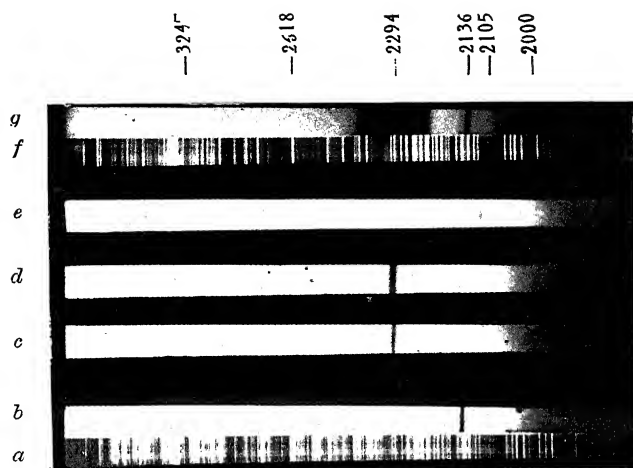
The other alternative for the photochemical process, viz.,



that is, the product of photochemical dissociation are not two normal atoms but a singly ionised Zinc and a negative Oxygen ion singly charged, appears to be excluded for the following reasons. It is evident that the electrostatic force is not completely destroyed and the potential energy curve for  $\text{Zn}^{+} \text{O}^{-}$  will be shown in B with a minimum. A photochemical process leading to such a transition as AB will be manifested as a band absorption. Up to this time, no trace of such absorption has been obtained.

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- a, f* ... Copper arc spectra.  
*e* ... Continuous spectrum.  
*b* ... Absorption spectrum of ZnO (in air).  
*c, d* ... Absorption spectra of CdO (in air).  
*g* ... Absorption spectrum of CdO (in air) at very high temperature showing the absorption of Cd<sub>2</sub> molecule.

# COLOUR AND CHEMICAL CONSTITUTION: THE EFFECT OF AUXOCHROMIC GROUPS ON PHTHALOPHENONE NUCLEUS.

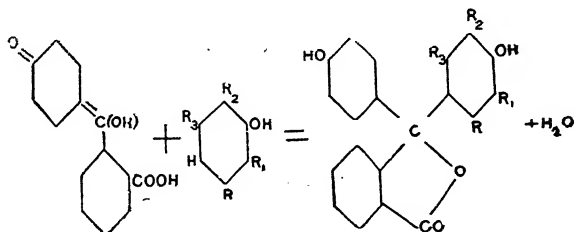
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Received March 21, 1933.

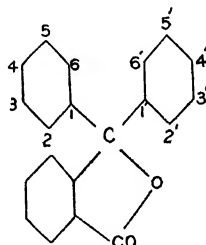
In a previous paper<sup>1</sup> by the present author fluoresceins and rhodamines of the mixed type were prepared by condensing 2:4-dihydroxy-benzoyl-benzoic acid with aromatic hydroxy and amino-hydroxy compounds, and the interesting derivatives of fluoran that were thus obtained were examined spectroscopically in order to arrive at a generalisation with respect to colour and constitution of these substances. It was found from a systematic examination of the absorption spectra of these compounds that the nearer a hydroxy or an amino group is to the pyrone oxygen atom of the molecule the greater is the intensity of the colour of the substance.

In the present paper the author has tried to study the problem from a slightly different point of view. Instead of preparing derivatives of fluoran as in the previous paper, hydroxy and amino-hydroxy derivatives of phthalophenone have been prepared by condensing *p*-hydroxy-benzoyl-benzoic acid with aromatic hydroxy and amino-hydroxy compounds thus :—



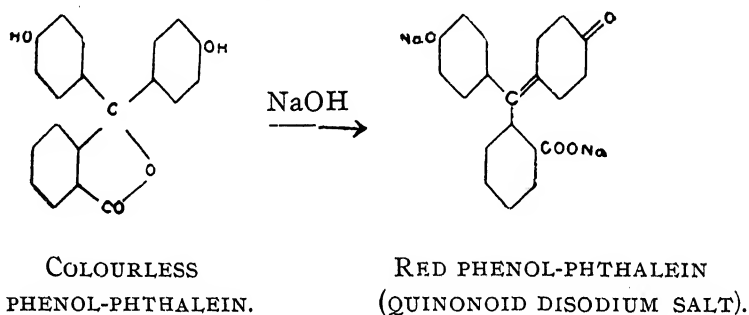
where R, R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> may be H, OH, NH<sub>2</sub>, N(CH<sub>3</sub>)<sub>2</sub>, N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>, etc. In constitution these substances are closely allied to phenol-phthalein and have chemical and physical properties similar to that substance. All of them dissolve in alkalies with a bright crimson colour with the exception of  $\alpha$ -naphthol derivative which develops a blue colour with these reagents. None of them have got any fluorescence in solution with the exception of the resorcinol derivative, which shows

the phenomenon in a very weak manner. From the point of view of absorption spectra it is found that the amount of colour development is practically dependent only on the load factor in the vicinity of the quinonoid linkage. *Para*-quinonoid compounds of the type derived from catechol, *ortho*-cresol or  $\alpha$ -naphthol are undoubtedly more coloured than the *ortho*-quinonoid compounds of the type derived from *p*-cresol, quinol,  $\beta$ -naphthol or 2:7-dihydroxy-naphthalene. The nomenclature of these substances can be arrived at by considering them as derivatives of phthalophenone,

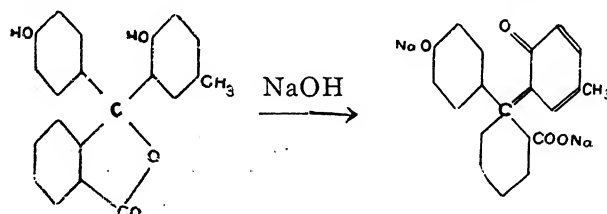


#### PHthalOPHENONE

just as phenol-phthalein itself can be regarded as 4:4'-dihydroxy-phthalophenone. In presence of alkali these substances, which are nearly always colourless in the solid state or in neutral solvents, develop intense colour due to the formation of a *para*-quinonoid structure as is well known in the classical example of phenol-phthalein, thus :—



An *ortho*-quinonoid structure is also possible in cases of *p*-cresol, quinol, etc., thus :—



The following aromatic hydroxy and amino-hydroxy compounds have been condensed with *p*-hydroxy-benzoyl-benzoic acid and the corresponding phthalophenone derivatives obtained: phenol, catechol, resorcinol, quinol, pyrogallol,



phloroglucinol, *o*-cresol, *m*-cresol, *p*-cresol, thymol, carvacrol,  $\alpha$ -naphthol,  $\beta$ -naphthol, 2 : 7-dihydroxy-naphthalene, *m*-dimethyl-amido-phenol and *m*-diethyl-amido-phenol. The absorption spectra and other properties of these compounds have been given in the form of a table at the end of the paper.

#### EXPERIMENTAL.

***p*-hydroxy-benzoyl-benzoic acid.**—It was prepared according to the method of Friedlander<sup>2</sup> from phenol-phthalein, via the oxime. 50 g. of phenol-phthalein was dissolved in 500 c.c. of 10 per cent caustic potash solution and to it was added 18 g. hydroxylamine hydrochloride. The mixture was gently heated over a small flame. The deep red colour gradually decreased and finally became yellow. On addition of some alcohol and acetic acid the oxime separated as a yellow compound. It was washed and dried. On crystallization from dilute alcohol it melted at 212° with decomposition.

The oxime was next digested with dilute sulphuric acid. On boiling the yellow colour vanished and whitish yellow crystals began to separate. It was allowed to cool. The crude *p*-hydroxy-benzoyl-benzoic acid thus obtained was crystallised from dilute alcohol and animal charcoal. It was obtained as white crystalline plates, m.p. 210° (yield 26 g.)

**4 : 4'-dihydroxy-phthalophenone.**—*p*-hydroxy-benzoyl-benzoic acid (15 g.) was heated with pure phenol (7.5 g.) and concentrated sulphuric acid (4 c.c.) in an oil bath maintained at 125° for two hours. The temperature was slowly raised to 140°. The condensed product was steam distilled to remove unacted phenol. The product was dissolved in dilute sodium hydroxide, filtered and precipitated by dilute hydrochloric acid when a white flocculent precipitate was obtained. On crystallization from alcohol it was obtained as colourless crusts (yield 11 g.)

**4 : 4' : 5'-trihydroxy-phthalophenone.**—It was obtained in a similar manner to the above by condensing *p*-hydroxy-benzoyl-benzoic acid and catechol in presence of sulphuric acid for 3 hours. The temperature was maintained as above (yield 41 %).

**4 : 4' : 6'-trihydroxy-phthalophenone.**—This substance was obtained from *p* hydroxy-benzoyl-benzoic acid and resorcinol in presence of concentrated sulphuric acid. The condensed product exhibited a green fluorescence in alkali solution. The fluorescence was considerably decreased in the purified product obtained on crystallization from alcohol (yield 58%).

**4 : 3' : 6'-trihydroxy-phthalophenone.**—It was obtained in a similar manner to the catechol compound by condensing *p*-hydroxy-benzoyl-benzoic acid with quinol. It was crystallized from dilute acetic acid (yield 49 %).

**4 : 3' : 4' : 5'-tetrahydroxy-phthalophenone.**—*p*-hydroxy-benzoyl-benzoic acid (9 g.), pyrogallol (6 g.) and concentrated sulphuric acid (2 c. c) was heated at 120°—130° for 6 hours. The condensation product was dissolved in absolute alcohol and

precipitated with petroleum ether. It was crystallised from glacial acetic acid (yield 46 %).

**4:2':4':6'-tetrahydroxy-phthalophenone.**—It was prepared by heating phloroglucinol and *p*-hydroxy-benzoyl-benzoic acid in presence of sulphuric acid for two hours at 150° and finally raising the temperature to 190°. It was crystallised from glacial acetic acid (yield 54 %)

**4:4'-dihydroxy-5'-methyl-phthalophenone.**—A mixture of 3 g. of the acid with 1.6 g. of *ortho*-cresol was heated for four hours at 130° with concentrated sulphuric acid as condensing agent. The melt was extracted with dilute caustic soda solution and precipitated with acetic acid. The phthalophenone was crystallised from dilute alcohol (yield 63 %)

**4:4'-dihydroxy-6'-methyl-phthalophenone.**—It was prepared from *meta*-cresol in a similar manner to the above with the only difference that it was heated for 8 hours (yield 52 %)

**4:6'-dihydroxy-3'-methyl-phthalophenone.**—This substance was obtained by heating *p*-hydroxy-benzoyl-benzoic acid and *para*-cresol for 9 hours at 125° in presence of strong sulphuric acid (yield 54 %)

**4:4'-dihydroxy-6'-methyl-3'-isopropyl-phthalophenone.**—A mixture of 2.5 g. of the acid, 1.8 g. of thymol and 3 g. of tin-tetrachloride was heated at 130°-35° for seven hours. The melt was extracted with dilute ammonia, filtered and the phthalophenone precipitated by acetic acid. It was crystallised from dilute alcohol (yield 49 %)

**4:4'-dihydroxy-3'-methyl-6'-isopropyl-phthalophenone.**—It was prepared from the acid and carvacrol in a similar manner to the above with the difference that it was heated for 8 hours at 130°. (yield 39 %)

**4:4'-dihydroxy-2':3'-phenylene-phthalophenone.**—A mixture of 2.5 g. of *p*-hydroxy-benzoyl-benzoic acid, 1.9 g. of  $\alpha$ -naphthol and 8 drops of concentrated sulphuric acid was heated for 8 hours at 140°. The melt was dissolved in dilute caustic soda solution and precipitated with acetic acid. The precipitate was crystallised from dilute alcohol. (yield 42%)

**4:6'-dihydroxy-3':4'-phenylene-phthalophenone.**—It was prepared from  $\beta$ -naphthol and the acid in a similar manner to the above (yield 39 %)

**4:6'-dihydroxy-3':4'(4'-hydroxy) phenylene-phthalophenone.**—This substance was prepared from 2:7-dihydroxy-naphthalene and *p*-hydroxy-benzoyl-benzoic acid in a manner similar to the above (yield 38 %)

**4:6'-dihydroxy-4'-dimethylamino-phthalophenone.**—A mixture of the acid (5 g.), *meta*-dimethylamido-phenol (3.6 g.) and concentrated sulphuric acid (1.5 g.) was heated at 135° for 4 hours. The melt was extracted with dilute sodium hydroxide solution and precipitated with dilute hydrochloric acid. The precipitate was crystallised from dilute alcohol (yield 57 %)

**4:6'-dihydroxy-4'-diethylamino-phthalophenone.**—This substance was prepared from *meta*-diethylamido-phenol and *p*-hydroxy-benzoyl-benzoic acid in a manner similar to the above (yield 55 %)

| Name (P=phthalophenone)                               | Appearance  | M. P.   | Colour in Caustic Soda solution. | Absorption maxima ( $\lambda$ ) | Analyses (Theoretical values in brackets). |
|---|-------------|---------|----------------------------------|---------------------------------|--|
| 1. 4:4'-dihydroxy-P ...                               | white       | 252°    | crimson red                      | 5560                            | {C=75.43 (75.49);<br>H=4.36 (4.40)}%.      |
| 2. 4:4':5'-trihydroxy-P ...                           | grey        | 148—49° | pink red                         | 5605                            | ...  |
| 3. 4:4':6'-trihydroxy-P ...                           | yellow      | 164°    | {red with green<br>fluorescence} | 5590                            | {C=71.46 (71.85);<br>H=4.02 (4.19)}%.      |
| 4. 4:3':6'-trihydroxy-P ...                           | white       | 153—55° | red                              | 5595                            | ...  |
| 5. 4:3':4':5'-tetrahydroxy-P ...                      | dirty white | 247—48° | Violet pink                      | 5575                            | ...  |
| 6. 4:2':4':6'-tetrahydroxy-P ...                      | white       | 256°    | red                              | 5660                            | {C=68.04 (68.57);<br>H=4.14 (4.00)}%.      |
| 7. 4:4'-dihydroxy-5'-methyl-P ...                     | "           | 117°    | "                                | 5730                            | {C=75.68 (75.90);<br>H=5.02 (4.82)}%.      |
| 8. 4:4'-dihydroxy-6'-methyl-P ...                     | "           | 131°    | pink                             | 5620                            | ...  |
| 9. 4:6'-dihydroxy-3'-methyl-P ...                     | "           | 135°    | "                                | 5615                            | ...  |
| 10. 4:4'-dihydroxy-6'-methyl-3'-iso-propyl-P ...      | dirty white | 231—32° | Violet-pink.                     | 5825                            | {C=76.54 (77.00);<br>H=5.86 (5.88)}%.      |
| 11. 4:4'-dihydroxy-3'-methyl-6'-iso-propyl-P ...      | "           | 178—79° | "                                | 5790                            | ...  |
| 12. 4:4'-dihydroxy-2':3'-phenylene-P                  | buff        | 171°    | blue                             | 6125                            | {C=77.86 (78.26);<br>H=4.36 (4.34)}%.      |
| 13. 4:6'-dihydroxy-3':4'-phenylene-P                  | pink        | 153°    | pink                             | 5605                            | ...  |
| 14. 4:6'-dihydroxy-3':4' (4''-hydroxy) phenylene-P .. | violet      | 261°    | Violet                           | 5635                            | {C=74.82 (75.00);<br>H=4.08 (4.16)}%.      |
| 15. 4:6'-dihydroxy -4'-dimethylamino-P                | pink-violet | 142°    | Violet-pink                      | 6030                            | ...  |
| 16. 4:6'-dihydroxy-4'-dimethylamino-P                 | "           | 93°     | "                                | 6060                            | {C=73.67 (74.03);<br>H=5.79 (5.91)}%.      |

The author expresses his best thanks to Dr. S. Dutt for his kind help and encouragement during the progress of the work.

*References :*

1. Ghatak and Dutt. *J. Indian Chem. Soc.*, 6, 465, 1929.
2. Friedlander, *Abs.*, *J. Chem. Soc.*, I, 273, 1893.

## CHEMICAL EXAMINATION OF THE ROOTS OF *THEVETIA NERIIFOLIA* (JUSS)

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Received March 21, 1933.

Every part of the plant of *Thevetia neriifolia* of the natural order *Apocynaceae* or yellow oleander as it is known in English and *pila-kaner* in Hindustani, is considered to have poisonous properties. The bark, leaves and roots of the plant have, therefore, been used in regulated doses as remedies for various ailments. In a previous paper<sup>1</sup> the results of examination of the seeds of the plant have been recorded. As no work has yet been done on the root of *Thevetia neriifolia*, its examination was undertaken with a view to study the nature of the chemical compounds contained in it. The analyses have proved the presence of a new hydrocarbon, some quantity of a wax, little volatile oil, some quantity of thevetin — a glucoside which has been recorded in the examination of the seeds and a considerable amount of the substance which yields Warden's<sup>2</sup> *thevetin-blue*. The results of examination have been recorded in the experimental part of the paper.

### Experimental

Fresh roots of *Thevetia neriifolia* was washed well of mud and other impurities and cut to small pieces by means of a chopper. The pieces were spread on paper and allowed to dry in air for three days. It was then found to contain 7.5 per cent of moisture and on incineration left 3.7 per cent of ash.

A preliminary examination of the roots showed the absence of alkaloids.

For complete analysis 2 kilos of the chopped and air dried roots were extracted with boiling rectified spirit in a round bottom extraction flask (capacity 5 litres). The filtrate on cooling deposited small quantity of a white flocculent precipitate. The precipitate was filtered and similar precipitates of subsequent extractions were collected together. On drying it weighed 14 g. The extraction of the roots was continued till the extract left only traces of residue on complete evaporation of the solvent. The combined extract was next concentrated under reduced pressure to one-third of its volume and on leaving overnight deposited a brown deposit. The precipitate on filtration and drying in a desiccator weighed 21g. The filtrate was again concentrated under reduced pressure to a volume of about 500 c. c. and was obtained as a brown syrupy liquid having a disagreeable odour. The first precipitate, second precipitate and the thick mother liquor were then separately analysed.

*First precipitate.*—The substance which was of a dirty white colour was extracted with boiling petroleum ether (b. p.  $35^{\circ}$ – $60^{\circ}$ ) and filtered. The filtrate on concentration deposited white needle-shaped soft crystals. The product on recrystallization from the same solvent and remaining in the vacuum desiccator for two days melted at  $79$ – $80^{\circ}$ . This substance burns with a non-luminous flame, which soon becomes luminous and on extinction of the flame gives out fumes having the characteristic smell of burnt paraffin. The molecular formula of this compound has been determined to be  $C_{13}H_{26}$ . No compound of this formula and possessing properties identical with it has hitherto been recorded in chemical literature. It is, therefore, proposed to designate the new compound *thevetene*, with reference to its properties of a hydrocarbon and the generic name of the plant from which it has been isolated.

*Thevetene.*—In ether, benzene, petroleum ether, carbon tetrachloride, chloroform, and ethyl alcohol it is sparingly soluble in the cold but dissolves in them to a small extent on heating. Thevetene is insoluble in pyridine, ethyl acetate and acetone. In concentrated sulphuric acid it turns slightly brown and on heating decomposes with charring. Concentrated and fuming nitric acids have no effect on the substance.

[Found : C, 85.28, 84.98, 85.39, 85.34; H, 14.32, 14.28, 14.37, 14.31; M. W. (ebulioscopic in benzene) 603, 599, 594, 610.  $C_{13}H_{26}$ , requires, C, 85.71, H, 14.28. M. W., 602.]

*Dibromo-thevetene.*—0.5 g. of the substance was dissolved in 50 c.c. pure carbon tetrachloride on boiling. To this was added 5 c.c. of carbon tetrachloride containing few drops of liquid bromine. The flask containing these substances was heated over water bath for five minutes and was then allowed to stand for spontaneous evaporation of the solvent. On complete evaporation of carbon tetrachloride a light brownish-yellow crust was left at the bottom. It was powdered and dried in a vacuum desiccator for three days when it melted at  $87$ – $88^{\circ}$ .

[Found : Br, 21.68 %;  $C_{13}H_{26}Br_2$ , requires, Br, 20.97%.]

*Second precipitate.*—The soft brown mass was extracted with cold ether (10°) several times till the extract was colourless. The residue on crystallization from benzene was obtained as white soft mass and was identified to be thevetene. The combined ethereal extract on distillation of the solvent left a brown waxy product possessing a disagreeable odour. This was steam distilled. When the distillate amounted to about 300 c.c., it was extracted with ether. The extract on complete removal of ether left about a c.c. of an oily substance having the characteristic odour of the original substance. The quantity of the oil being too small, it could not be further analysed. The product left in the flask after steam distillation was identified to be a wax.

*The thick brown mother liquor.*—It was distilled under reduced pressure (10 mm.) till it was obtained as a soft solid mass. It was then extracted several times with ether to remove the oily and waxy contaminations. The product was then extracted with boiling chloroform. The chloroform extract on complete removal of the solvent left small quantity of a brown pasty solid (about 2 g.). It was soluble in ethyl acetate. The substance was twice crystallized from dilute alcohol and animal charcoal, when it was obtained as white slender needles melting at 192°. It was identified to be thevetin, a glucoside which was isolated and described in the paper<sup>1</sup> on the examination of the seeds of *Thevetia neriifolia*.

The residue left after chloroform extraction readily reduced Fehling's solution, Tollens reagent and ammoniacal silver nitrate. The whole mass was dissolved in 400 c.c. of water and to it was added lead acetate solution. The precipitate, which was of a yellowish-white colour, was filtered off and the filtrate was reprecipitated with saturated solution of tannic acid. The filtrate was freed from tannic acid by barium hydroxide solution and filtered. Excess of barium in the solution was removed by passing a current of carbon dioxide in it. The filtrate now became very light brown in colour. A little of this solution on treatment with concentrated hydrochloric acid developed greenish-blue colour and on warming deposited a flocculent precipitate of brown colour. This compound corresponded to Warden's<sup>2</sup> *thevetin-blue*, a reference of which has already been made in a previous communication. Every attempt to separate the compound, which developed greenish-blue colour, in a pure form was unsuccessful. The whole of the mother liquor was, therefore, warmed with a few c.c. of concentrated hydrochloric acid and the brown precipitate was filtered and washed free from soluble impurities. On drying it became brown black in colour and weighed 6.4 g. It does not melt even on heating to 300°. This substance is insoluble in all organic solvents excepting pyridine, in which it dissolves with a brown colour. From the pyridine solution it was precipitated by addition of water and was obtained as a brown-black amorphous powder. It does not contain nitrogen. This substance has been named *neriifolin*, with reference to the specific name of the plant from which it has been isolated. On combustion the substance was found to contain C=60.8% and H=4.64%. The only

derivative of this substance that could be prepared was the reduced and simultaneously acetylated one.

*Reduced and acetylated neriifolin.*—3 g. of neriifolin, 8 g. of finely powdered zinc dust and 50 c.c. acetic anhydride were put in a flask and put under reflux. Few drops of water were added when the evolution of hydrogen started. It was then gently heated. When the reaction slowed down few drops of water were again added. The operation was repeated several times till the zinc dust was completely used up. It was then filtered hot. The filtrate on dilution and neutralization with ammonia gave a brown pasty deposit at the bottom which slowly solidified. It was crystallized from alcohol and animal charcoal. A micro-crystalline white powder was obtained which melted at 93°. This substance gave pink and yellow colour reactions with concentrated sulphuric and nitric acids respectively.

On combusting the substance the following results were obtained: C=63.52% and H=7.04%.

Our best thanks are due to Dr. S. Dutt, for his kind interest in the work.

#### *References.*

<sup>1</sup> Ghatak, *Bull. Acad. Sci., U. P.*, 79, 2, 1932.

<sup>2</sup> Warden, *Brit. Chem. Abs.*, II, 1126, 1882



# ON THE MAXIMUM MODULUS PRINCIPLE

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Received February 1, 1933.

1. In a recent joint paper<sup>1</sup> of ours we have studied the singularities of the function  $f(s)$  defined by the Laplace-Abel integral

$$\int_0^{\infty} \phi(z) e^{-sz} dz,$$

where  $\phi(z)$  is an analytic function of  $z (= \rho e^{i\psi})$  of exponential type in the angular region  $|\psi| \leq \alpha$ ,  $\alpha > 0$ . The results obtained in this paper have now enabled us to establish the following theorem which is the main purpose of this note.

*Theorem I—*

*If*

(1.1)  $\phi(z)$  be an analytic function of  $z$  in the angle  $|\psi| \leq \alpha < \frac{\pi}{2}$ , and satisfy the relation  $\phi(z) = O(e^{M\rho})$ , ( $M > 0$ ), throughout this angle;

(1.2) the integral  $\int_0^{\infty} |\phi(\rho e^{\pm i\alpha})| d\rho$  be convergent;

then  $\phi(z) = O(e^{\epsilon\rho})$  throughout the region  $|\psi| \leq \alpha$ ,  $\epsilon$  being any positive number howsoever small.

This result is analogous to a well-known theorem of Phragmén-Lindelöf,<sup>2</sup> which differs from it only in having in place of (1.2)

(1.3)  $\phi(z) = O(1)$  on the boundary lines  $\psi = \pm \alpha$ , and in proving that  $\phi(z)$  is bounded throughout the angular region

It is obvious that (1.3) does not imply (1.2). To see that the convergence of  $\int_0^{\infty} |F(x)| dx$  does not imply that  $F(x) = O(1)$ , take  $F(x) = \frac{x^2}{1+x^7 \sin^2 x}$ . Here

$\int_0^{\infty} |F(x)| dx$  is convergent<sup>3</sup>, but  $F(x)$  is not bounded as  $x \rightarrow \infty$ . In fact, at points on the  $x$ -axis  $F(x)$  is as large as  $x^2$ . It follows, therefore, that neither of (1.2)

and (1.3) implies by itself the other, and so none of the above two theorems seems included in the other.

## 2. Proof of Theorem I.

Let  $\phi(0)=c$ , and let

$$\phi_1(z) \equiv \phi(z) - c.$$

Consider the function defined by

$$f(s) = \int_0^{\infty} \phi_1(z) e^{-sz} dz.$$

Proceeding as in theorem I of our paper<sup>1</sup>,  $f(s)$  can be proved to be an analytic function of  $s (=re^{i\theta})$  in the interior of the angular region bounded by the radii vectores  $\theta = \pm \left( \frac{\pi}{2} + \alpha \right)$ , and of order  $\left( \frac{1}{|s|^2} \right)$  throughout the same region.

Conversely, applying theorems II and III of our paper<sup>1</sup>, we can show that  $\phi_1(z)$  is an analytic function of  $z$  in the angular region  $|\psi| \leq \alpha$ , and satisfies throughout that region the relation  $\phi(z) = O(e^{\epsilon\rho})$ ,  $\epsilon$  being any positive number howsoever small.

Now

$$\begin{aligned} |\phi(z)| &= |\phi_1(z) + c| \\ &\leq |\phi_1(z)| + |c| \\ &= O(e^{\epsilon\rho}) + |c| \\ &= O(e^{\epsilon'\rho}) \end{aligned}$$

where  $\epsilon'$  is another arbitrarily small positive number.

*Corollary.* If  $\phi(z)$  be an analytic function of exponential type in an angular region including the ray  $\psi = \alpha$ ,

and  $\int_0^{\infty} |\phi(\rho e^{i\alpha})| d\rho$  be convergent, then,  $\phi(\rho e^{i\alpha}) = O(e^{\epsilon\rho})$ .

This can be proved in the same manner as theorem I.

3. An immediate consequence of theorem I is the following theorem.

*Theorem II—*

If  $\phi(z)$  satisfies (1.1), and

$$3.1 \quad \int_0^{\infty} |\phi(\rho e^{\pm i\alpha})| e^{-k\rho} d\rho \text{ is convergent, } (k > 0);$$

$$\text{then } \lim_{\rho \rightarrow \infty} \frac{\log |\phi(\rho e^{i\psi})|}{\rho} \leq k \sec \alpha \cos \psi \text{ for } |\psi| \leq \alpha.$$

Let  $\phi(z) \equiv \phi_1(z) e^{zk \sec \alpha}$ . Then  $\phi_1(z)$  satisfies the conditions of Theorem I, and consequently

$$\phi_1(z) = O(e^{\epsilon \rho}) \text{ throughout } |\psi| \leq \alpha.$$

$$\text{Hence } \lim_{\rho \rightarrow \infty} \frac{\log |\phi(\rho e^{i\psi})|}{\rho} \leq k \sec \alpha \cos \psi.$$

4. Similar analysis enables us to suggest new proofs of the well-known theorems of Riesz and Carlson<sup>4</sup>. Take, for instance, Riesz's theorem which is as follows:—

If

$$(4.1) \quad \phi(z) \text{ is analytic in the half-plane } R(z) \geq 0, \text{ and is of exponential type;}$$

$$(4.2) \quad \phi(z) = O(e^{-\delta \rho}), \delta > 0, \text{ on the imaginary axis;}$$

then  $\phi(z) \equiv 0$ .

$$\text{Consider } f(s) = \int_0^\infty \phi(z) e^{-sz} dz.$$

Then proceeding as in theorem I of our paper<sup>1</sup>,  $f(s)$  can be proved to be an integral function of  $s$  and of order  $\left(\frac{1}{|s|}\right)$  as  $|s| \rightarrow \infty$  and so  $f(s) \equiv 0$ .

Hence  $\phi(z) \equiv 0$ .

To prove Carlson's theorem, consider the function  $g(z) \equiv \frac{\phi(z)}{\sin \pi z}$ , and apply Riesz's theorem to  $g(z)$ .

5. Mittag-Leffler<sup>5</sup> has given some examples of integral functions defined by means of Taylor's series which tend to zero uniformly in the whole plane except in an arbitrarily small angular region. We take this opportunity of pointing out that such functions can also be defined by means of the Laplace-Abel integral.

Suppose  $\phi(z)$  is an analytic function of  $z$  in the half-plane  $R(z) \geq 0$ , and  $\phi(z) = O(e^{\epsilon \rho})$  for every positive  $\epsilon$  throughout the half-plane. Suppose further that for some values of  $\psi$ , say,  $\psi = 0$ ,  $\phi(\rho e^{i\psi}) = O(e^{-\Delta \rho})$ , where  $\Delta$  is any arbitrarily positive number howsoever large. An example of such a function  $\phi(z)$  is

$\frac{1}{[\log(z+\beta)]^\beta}$ , where  $\beta > 1$ , and  $[\log(z+\beta)]^\beta$  has its principal value. Then  $f(s)$

defined by  $\int_0^\infty \phi(z) e^{-sz} dz$  will be an integral function of  $s$ , and outside the strip

$|t| \leq \delta, \sigma \leq \delta'$ , where  $\delta$  and  $\delta'$  are any positive numbers howsoever small, it will be of order  $\frac{1}{|s|}$  so that it will tend to zero as  $|s| \rightarrow \infty$  uniformly in the whole region except the above-mentioned strip.

Further, we may observe that the order of  $f(s)$  in the strip must be greater than that of  $e^{kp}$ , unless  $\phi(z) \equiv 0$ . For if  $f(s) = O(e^{kp})$  in this strip, and is bounded throughout the rest of the plane, then  $f(s)$  must reduce to a constant, which must be zero here. That is,  $f(s) \equiv 0$ , and so  $\phi(z) \equiv 0$ . This is a contradiction.

#### *References.*

- <sup>1</sup> Srivastava and Jain : *Bul. Acad. Sci., U. P.*, 2, 53, 1932.
- <sup>2</sup> Phragmén and Lindelöf : *Acta Mathematica*, 31, 381, 1908.
- <sup>3</sup> Bromwich : *Infinite Series*, pp. 469-470 (2nd Ed.).
- <sup>4</sup> M. Riesz : *Proc. Camb. Phil. Soc.*, 20, 205, 1920.
- <sup>5</sup> Lindelöf : *Calcul des Residues*, pp. 119-121.

# BUSINESS MATTERS

PATRON

His Excellency Sir W. Malcolm Hailey, G.C.I.E., K.C.S.I., I.C.S.  
*The Governor of the United Provinces of Agra and Oudh.*

HONY. FELLOWS

The Hon'ble Mr. J. P. Srivastava, M.Sc. (Tech.)  
*The Minister of Education,*  
*The United Provinces of Agra and Oudh.*

Pandit Madan Mohan Malaviya, LL.D.  
*Vice-Chancellor,*  
*Benares Hindu University, Benares.*

# Business Supplement

## ANNUAL MEETING

The Annual Meeting of the Academy of Sciences was held in the Vizianagram Hall, Muir College Buildings, Allahabad, at 3 p.m. on Friday, January 13, 1933. The Hon'ble Mr. J. P. Srivastava, M.Sc. (Tech.), Education Minister, presided over the function. On account of unavoidable absence of Professors P. S. MacMahon and A. C. Banerji, the General Secretaries, Dr. P. L. Srivastava read the Annual Report of the Academy of Sciences.

Prof. M. N. Saha, the President of the Academy, read his address. The Hon'ble Mr. J. P. Srivastava then delivered his speech.

Prof. K. N. Bahl, proposed a vote of thanks to the Hon'ble Minister and Prof. N. R. Dhar seconded the vote of thanks.

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## SECRETARIES' REPORT

WE HAVE the honour to submit the following report on the working of the Academy during the period beginning from the 1st of January, 1932, and ending on the 31st of March, 1933 :—

The most notable event of the year under review was the inaugural meeting of the Academy, which was held in the Vizianagram Hall, Muir Central College Buildings, Allahabad, on Tuesday, March 1, 1932. The success of the function was mainly due to the inspiring presence of His Excellency Sir Malcolm Hailey, G.C.I.E., K.C.S.I., I.C.S., the Patron of the Academy, who presided over the meeting. His Excellency takes a keen personal interest in the affairs of the Academy, and has been pleased to sanction a non-recurring grant of Rs. 2,000 to the Academy for the current financial year.

The Academy has now on its roll 102 members, of whom nineteen are non-resident members. Pandit Madan Mohan Malaviya, Vice-Chancellor of the Benares Hindu University, has been elected an Honorary Fellow of the Academy in recognition of his eminent services in the cause of science and education in these Provinces. Three new Fellows, *viz.*, Dr. Rudolf Samuel, Dr. Robert F. Hunter, and Dr. P. L. Srivastava, have also been elected. We have to report, with great regret, that the Academy had to mourn the loss, by death, of two members of the Academy, *viz.*, Mr. Nabendu Bhushan Banerji, a promising young member of the Academy, and Dr. W. Dudgeon, a botanist of repute.

The Academy has decided that some of its ordinary meetings may also be held at other University and educational centres where there is a sufficient number of members to form a quorum and where the members are prepared to make necessary arrangements for the meeting. For the convenience of the Christian members of the Academy the meetings are generally held on week days. During the period under review 43 papers were read.

The Academy is indebted to Mr. W. G. P. Wall, M.Sc., I.E.S., Assistant Director of Public Instruction, U.P., for his generous gift of a large number of volumes of different scientific journals to the Academy. The Academy has already published the first volume as well as first and second parts of the second volume of its Bulletin. It has received good recognition in India as well as outside India, and we are already receiving 53 foreign and Indian scientific journals in exchange. The work done by the Academy has attracted the attention of the scientific world. NATURE, the premier scientific journal of Great Britain, welcomes, in its issue of October 8, 1932, the successful inauguration of the Academy, and feels little doubt that the future success of the Academy is assured, and that it will do much to stimulate the research spirit in the Universities of the United Provinces of Agra and Oudh. The need for a building of the Academy is urgently felt. With the help of the Government, the Universities of these Provinces, and generous public we hope that it will be possible for us to construct a building for the Academy before long.

The secretaries wish to express their thanks to Dr. D. R. Bhattacharya, Hony. Treasurer, for his ungrudging help and active co-operation.

### ABSTRACTS OF THE PROCEEDINGS

The list of the Office-Bearers and Members of the Council to which the management of the affairs of the Academy was entrusted for the year 1932-33 is given in appendix A.

Appendix B contains the list of names of 102 members who were on the roll of the Academy on March 31, 1933.

The Council expressed its deep gratitude to the Government for the Non-recurring grant of Rs. 2,000 awarded to the Academy for the year 1932-33.

The Council gratefully accepted the generous offer of the Hon'ble Mr. J. P. Srivastava, M. Sc. (Tech.), Education Minister, to found a Gold Medal to be awarded to the author of the best paper read before the Academy in any year.

The Council accepted with thanks the generous gift of 59 volumes of different scientific journals to the Academy from Mr. W. G. P. Wall, M. Sc., I. E. S., Assistant Director of Public Instruction of the United Provinces.

Pandit Madan Mohan Malaviya, B. A., LL. D., Vice-Chancellor, Benares Hindu University was elected an Honorary Fellow of the Academy of Science, U. P. on account of his eminent services for the cause of education and science, on the 6th of August, 1932.



The following three members were elected Fellows of the Academy in the Fellow's meeting held on November 30, 1932.

1. Prof. Dr. Rudolf Samuel, Ph. D., Muslim University, Aligarh. U. P.
2. Prof. Dr. Robert F. Hunter, D. Sc., Ph. D., Muslim University, Aligarh, U P.
3. Dr. P. L. Srivastava, M A., D. Phil., Allahabad University, Allahabad.

The following members were elected Office-Bearers and the Members of the Council for the year 1933 in the Annual meeting held on January 13, 1933.

**President:**

1. Prof. K. N. Bahl, D.Phil., D.Sc.

**Vice-Presidents :**

2. Prof. M. N. Saha, D.Sc., F.R.S., F.A.S.B., F.Inst.P., P R.S.
3. Prof. B. Sahni, D.Sc., Sc. D., F.L.S., F.A.S.B.

**Hony. Treasurer :**

4. Prof. D. R. Bhattacharya, M.Sc., Ph.D., D.Sc, F.Z. S.

**General Secretaries :**

5. Prof. P. S. MacMahon, B.Sc., M.Sc., F.I.C.
6. Prof. A. C. Banerji, M.A., M Sc., F.R A.S., I.E.S.

**Foreign Secretary :**

7. Prof. N. R. Dhar, D.Sc, F I.C., I.E.S.

**Other Members of the Council :**

8. Prof. K. C. Mehta, Ph. D, M.Sc.
9. Dr. S. S. Nehru, M.A, Ph.D., I.C.S., M.L.C.
10. Prof. Ch. Wali Mohammad, M.A, Ph.D., I.E.S.
11. Prof. K. K. Mathur, B Sc., A R.S.M.
12. Dr. P. L. Srivastava, M.A., D.Phil.
13. Prof. Robert F. Hunter, D.Sc, Ph.D.
14. Dr. S. M. Sane, B.Sc., Ph.D.
15. Prof. C. Maya Das, B.Sc, M A., I.A.S
16. Prof. K. C. Pandya, D.Sc.

## APPENDIX A

### LIST OF OFFICE-BEARERS AND MEMBERS OF THE COUNCIL.

1932

#### President :

1. Prof. M. N. Saha, D.Sc. (Cal.), F.R.S., F.A.S.B., F. Inst. P, P. R. Scholar, Professor of Physics, Allahabad University, Allahabad.

#### Vice-Presidents :

2. Prof. N. R. Dhar, D.Sc. (Lond.), Docteur ès Sciences (Paris), F.I.C., I.E.S., Professor of Chemistry, Allahabad University, Allahabad.
3. Prof. K. N. Bahl, D. Phil. (Oxon.), D. Sc. (Punjab), Professor of Zoology Lucknow University, Lucknow.

#### Hony. Treasurer :

4. Prof. D. R. Bhattacharya, M.Sc. (All.), Ph. D. (Dublin), Docteur ès Sciences (Paris), Professor of Zoology, Allahabad University, Allahabad.

#### General Secretaries :

5. Prof. P. S. MacMahon, B.Sc., (Oxon), M.Sc. (Manchester), F.I.C., Professor of Chemistry, Lucknow University, Lucknow.
6. Prof. A. C. Banerji, M.Sc. (Cal.), M.A. (Cantab), F.R.A.S. (Eng.), I. E. S., Professor of Mathematics, Allahabad University, Allahabad.

#### Foreign Secretary :

7. Prof. Ch. Wali Mohammad, B.A. (Cantab), Ph. D. (Göttingen), I. E. S. Professor of Physics, Lucknow University, Lucknow.

#### Other Members of the Council :

8. Prof. K. C. Mehta, Ph.D. (Cantab), M. Sc. (Punjab), Professor of Botany, Agra College, Agra.
9. Dr. S. S. Nehru, M.A., Ph.D., I.C.S., M.L.C., Deputy Secretary to Government, U.P., Publicity Department, Lucknow.
10. Prof. H. D. H. Drane, M.Sc., Ph.D., A.M.I.E.E., A.M.I. Chem. E., Principal, Harcourt Butler Technological Institute, Cawnpore

11. Prof. K. K. Mathur, B.Sc. (Hons., Lond.), A.R.S.M., Professor of Geology, Benares Hindu University, Benares.
12. Dr. Luxmi Narayan, D.Sc., (All.), Reader in Mathematics, Lucknow University, Lucknow.
13. Dr. D. N. Forman, M.D., Jumna Mission Dispensary, Allahabad City.
14. Prof. B. Sahni, D.Sc. (Lond.), Sc.D. (Cantab), F.L.S., F.A.S.B., Professor of Botany, Lucknow University, Lucknow.
15. Dr. P. L. Srivastava, M.A., D.Phil. (Oxon), Reader in Mathematics, Allahabad University, Allahabad.
16. Prof. André Weil, Docteur ès Sciences (Paris), 3. Rue Auguste—Comte, Paris '6c', France.

## APPENDIX B

### ORDINARY MEMBERS

R—Resident. N—Non-Resident.

\*—Denotes a Fellow.

| Date of Election. |    |  |
|-------------------|----|--|
| 17-4-1931         | R  | Asundi, (R.K.), Ph.D., Reader, Physics Department, Muslim University, Aligarh.                                 |
| 21-12-1931        | N  | Bagchi, (S.C.), B.A., L.L.D., Principal, Law College, Calcutta.  |
| 1-1-1930          | R* | Bahl, (K.N.), D. Phil., D.Sc., Professor of Zoology, Lucknow University, Lucknow.                              |
| 1-1-1930          | R* | Banerji, (A.C.), M.A., M.Sc., F.R.A.S., I.E.S., Professor of Mathematics, Allahabad University, Allahabad.     |
| 29-2-1932         | R  | Banerji, (G.N.), The Scientific Instrument Company Ltd., Albert Road, Allahabad.                               |
| 22-12-1932        | N  | Banerji, (S.K.), D.Sc., Meteorological Office, Ganeshkhind Road, Poona 5.                                      |
| 17-4-1931         | N  | Basu, Saradindu, M.Sc., Meteorologist, Ganeshkhind Road, Poona 5.  |
| 19-3-1931         | R  | Bhargava, Saligram., M.Sc., Reader, Physics Department, Allahabad University, Allahabad.                       |
| 17-4-1931         | R  | Bhargava, Vashishta, M.Sc., I.C.S., Assistant Magistrate and Collector, Budaun.                                |
| 17-4-1931         | R  | Bhatia, (K.B.), I.C.S., Joint Magistrate, Shahjahanpur.  |
| 1-1-1931          | R* | Bhattacharya, (D.R.), M.Sc., Ph.D. Docteur ès Sciences, Professor of Zoology, Allahabad University, Allahabad. |
| 17-4-1931         | R  | Bhattacharya, (D.P.), M.Sc., Bareilly College, Bareilly.   |
| 3-4-1933          | R  | Chand, Tara, M. A., D.Phil., Principal, K. P. University College, Allahabad.                                   |
| 29-2-1932         | R  | Charan, Shyama, M.A., M.Sc., (Lond), Agra College, Agra.   |
| 1-1-1930          | R* | Chatterji, (G.), M.Sc., Meteorologist, Upper Air Observatory, Agra.  |
| 17-4-1931         | R  | Chatterji, (K.P.), M.Sc., A.I.C., F.C.S., Reader, Chemistry Department, Allahabad University, Allahabad.       |
| 17-4-1931         | R  | Chatterji, (A.C.), D.Sc., Chemistry Department, Lucknow University, Lucknow.                                   |
| 19-3-1931         | R  | Chaudhury, Rabindra Nath, M.Sc., M.A., Mathematics Department, Allahabad University, Allahabad.                |

Date of  
Election.

Alphabetical List of Ordinary Members

|            |    |   |
|------------|----|---|
| 17-4-1931  | R  | Chaudhury, (H.P.), M.Sc., Lucknow University, Lucknow.  |
| 19-3-1931  | R  | Das, Ramsaran, D.Sc., Zoology Department, Allahabad University, Allahabad.  |
| 17-4-1931  | R  | Das, C. Maya, M.A., B.Sc., I.A.S., Principal, Agricultural College, Cawnpore.   |
| 28-10-1932 | N  | Das, (A.K.), D.Sc., Alipore Observatory, Alipore, Calcutta.   |
| 22-12-1932 | N  | Das, (B.K.), D.Sc., Professor of Zoology, Osmania University, Hyderabad, Deccan.  |
| 15-9-1931  | R  | Dasannacharya, (B.), Ph.D., Professor of Physics, Benares Hindu University, Benares.                                      |
| 17-4-1931  | R  | Deodhar, (D.B.), Ph.D., Reader, Physics Department, Lucknow University, Lucknow.  |
| 17-4-1931  | R  | Dey, (P.K.), M.Sc., I.A.S., Plant Pathologist to Government, United Provinces, Nawabganj, Cawnpore.                       |
| 29-2-1932  | R  | Deb, Suresh Chandra, D.Sc., Physics Department, Allahabad University, Allahabad.  |
| 1-1-1930   | R* | Dhar, (N.R.), D.Sc., Docteur ès Sciences, F.I.C., Professor of Chemistry, Allahabad University, Allahabad.                |
| 1-1-1930   | R* | Drane, (H.D.H.), M.Sc., Ph.D., A.M.I.E.E., A.M.I. Chem. E., Principal, Harcourt Butler Technological Institute, Cawnpore. |
| 17-4-1931  | R  | Dudgeon, (W.), Ph.D., Ewing Christian College, Allahabad.   |
| 19-3-1931  | R  | Dutt, (S.K.), M.Sc., Zoology Department, Allahabad University, Allahabad.   |
| 17-4-1931  | R  | Dutt, (S.B.), D.Sc., Reader, Chemistry Department, Allahabad University, Allahabad.                                       |
| 28-10-1932 | R  | Dutt, (A.K.), M.Sc., Benares Hindu University, Benares.   |
| 17-4-1931  | R  | Forman, (D.N.), M.D., Jumna Dispensary, Allahabad.  |
| 22-2-1933  | R  | Ghatak, Narendranath, M. Sc, Chemistry Department, Allahabad University, Allahabad.                                       |
| 19-3-1931  | R  | Ghosh, (R.N.), D.Sc., Physics Department, Allahabad University, Allahabad.  |
| 19-3-1931  | R  | Ghosh, Satyeshwar, D.Sc., Chemistry Department, Allahabad University, Allahabad.  |
| 19-4-1931  | R  | Ghosh, (B.N.), M.Sc., St. Andrew's College, Gorakhpur.  |
| 15-9-1931  | N  | Gogate, (D.V.), M.A., Baroda College, Baroda.   |
| 15-9-1931  | R  | Gordon, (C.B.), B.A., Christ Church College, Cawnpore.  |
| 17-4-1931  | R  | Gupta, (B.M.), D.Sc., Deputy Public Analyst to Government, United Provinces, Lucknow.                                     |
| 21-12-1931 | R  | Hansen, (W.J.), M.A., Allahabad Agricultural Institute, Naini, E.I.R., Allahabad.   |

Date of  
Election.

## Alphabetical List of Ordinary Members

- 17-4-1931 R Higginbottom, Sam, D. Phil., Principal, Allahabad Agricultural Institute, Naini, E.I.R. (Allahabad).
- 17-4-1931 R\* Hunter, Robert (F.), D.Sc., Ph.D., Professor of Chemistry, Muslim University, Aligarh.
- 21-12-1931 R Joshi, (S.S.), D.Sc., Professor of Chemistry, Benares Hindu University, Benares.
- 15-9-1931 N Kichlu, (P.K.), D.Sc., Department of Physics, Government College, Lahore.
- 1-1-1930 R\* King, (C.A.), B.Sc., (Hons.) A.R.C.Sc., M.I.M.E, Principal, Engineering College, Benares Hindu University, Benares.
- 17-4-1931 R Koshambi, (D.D.), M.A., Department of Mathematics, Muslim University, Aligarh.
- 1-1-1930 R\* Luxmi Narayan, D.Sc, Reader, Mathematics Department, Lucknow University, Lucknow.
- 1-1-1930 R\* MacMahon, (P.S.) B.Sc. (Hons.), M.Sc. Professor of Chemistry, Lucknow University, Lucknow.
- 1-1-1930 R\* Mathur, (K.K.), B.Sc. (Hons.), A.R.S.M., Professor of Geology, Benares Hindu University, Benares.
- 1-1-1930 R\* Mehta, (K.C.), Ph.D., M.Sc., Agra College, Agra.
- 1-1-1930 R\* Mitter, (J.H.), M.Sc., Ph.D., Professor of Botany, Allahabad University, Allahabad.
- 15-9-1931 R Mathur, (L.P.), M.Sc., St. John's College, Agra.
- 19-3-1931 R Mazumdar, Kanakendu, D.Sc., Physics Department, Allahabad University, Allahabad.
- 19-3-1931 R\* Mehra, (H.R.), Ph.D., Reader, Zoology Department, Allahabad University, Allahabad.
- 21-12-1931 R Mehta, (N.C.), I.C.S., Director of Agriculture, United Provinces, Lucknow.
- 17-4-1931 R Mukerjee, (S.K.), M.Sc., Agra College, Agra.
- 17-4-1931 R Mukerjee, (S.K.), D.Sc. Reader, Botany Department, Lucknow University, Lucknow.
- 22-2-1933 R Narliker, (V. V.), M.A., Professor of Mathematics, Benares Hindu University, Benares.
- 17-4-1931 R Nehru, (S.S.), M.A., Ph.D., I.C.S., M.L.C., Deputy Secretary to Government, U. P., Publicity Department, Lucknow.
- 17-4-1931 R Pandya, (K.C.), D.Sc., St. John's College, Agra.
- 3-4-1933 N Parija, (P. K.), M.A., I.E.S., Ravensha College, Cuttack.
- 15-9-1931 N Prasad, Mata, D.Sc., Royal Institute of Science, Bombay.
- 3-4-1933 R Prasad, Badrinath, Ph.D., Docteur ès Sciences, Mathematics Deptt., Allahabad University, Allahabad.

Date of  
Election.

Alphabetical List of Ordinary Members

|            |    |  |
|------------|----|--|
| 17-4-1931  | R  | Puri, (B D ), M A., Thomason Civil Engineering College, Roorkee.   |
| 22-12-1932 | N  | Qureshi, (M.), M.Sc., Ph.D., Professor, of Chemistry, Osmania University College, Hyderabad, Deccan.             |
| 3-4-1933   | R  | Raja Ram, M.A., B.E., Principal of Civil Engineering, Thomason College, Roorkee, U. P.                           |
| 19-3-1931  | R  | Ranjan, Shri, M.Sc., Docteur ès Sciences, Reader, Botany Department, Allahabad University, Allahabad.            |
| 15-9-1931  | N  | Rao, A. Subba, D.Sc Medical College, Mysore.   |
| 22-2-1933  | N  | Rao, G. Gopala, B.A., M.Sc., Chemistry Department, Andhra University, Waltair.                                   |
| 21-12-1931 | R  | Rao, D. H. Ramchandra, B.E., A.M.I.E., Engineer, Allahabad University, Allahabad.                                |
| 22-2-1933  | N  | Ray, Bidhubhusan, D.Sc., 92 Upper Circular Road, Calcutta.   |
| 21-12-1931 | R  | Ray, Satyendra Nath, M.Sc., Physics Department, Lucknow University, Lucknow.                                     |
| 1-1-1930   | R* | Richards, (P.B.), A.R.C.S., F.E.S., Entomologist to the Government, United Provinces, Cawnpore.                  |
| 1-1-1930   | R* | Saha, (M.N.), D.Sc, F.R.S., F.A.S.B, F. Inst. P., P.R.S., Professor of Physics, Allahabad University, Allahabad. |
| 29-2-1932  | R  | Saha, Jogendra Mohan, M.Sc., Manager, Srikrishna Desi Sugar Works, Jhusi, (Allahabad).                           |
| 1-1-1930   | R* | Sahni, (B.), D.Sc., Sc.D., F.L.S., F.A.S.B., Professor of Botany, Lucknow University, Lucknow.                   |
| 17-4-1931  | R* | Samuel, Rudolf, Ph.D., Professor of Physics, Muslim University, Aligarh.   |
| 17-4-1931  | R  | Sane, (S.M.), B.Sc., Ph.D., Reader, Chemistry Department, Lucknow University, Badshah Bagh, Lucknow.             |
| 21-12-1931 | R  | Sathe, (J.L.), I.C.S., Finance Secretary to Government, U. P., No. 1, Secretariat Quarters, Lucknow.             |
| 3-4-1933   | R  | Sen, (K. C.), D.Sc., Imperial Institute of Veterinary Research, Muktesar, Kumaun.                                |
| 17-4-1931  | R  | Seth, (S.D.), M.Sc., Christ Church College, Cawnpore.  |
| 1-1-1930   | R* | Sethi, (R.L.), M.Sc., M.R.A.S., Economic Botanist to Government, United Provinces, Cawnpore.                     |
| 19-3-1931  | R  | Sethi, Nihal Karan, D.Sc., Agra College, Agra.   |
| 15-9-1931  | R  | Sharma, Ram Kishore, M.Sc., Physics Department, Ewing Christian College, Allahabad.                              |
| 3-4-1933   | N  | Siddiqi, (M. R.), Ph.D., Professor of Mathematics, Osmania University, Hyderabad, Deccan.                        |

Date of  
Election

Alphabetical List of Ordinary Members

- 3-4-1933 R Siddiqui, Mohd. Abdul Hamid, M. B. B.S., M. S., F.R.C.S.,  
D. L. O., Professor of Anatomy, King George's Medical College,  
Lucknow.
- 17-4-1931 R Singh, Avadesh Narain, D.Sc., Department of Mathematics, Luck-  
now University, Lucknow.
- 17-4-1931 N Sbonawala, (M. F.), M.Sc., Maharaja's College, Jaipur (Rajputana).
- 19-3-1931 R\* Srivastava, (P. L.), M.A., D.Phil., Reader, Mathematics Department,  
Allahabad University, Allahabad.
- 15-9-1931 N Srikantia, (C.), B.A., D.Sc., Medical College, Mysore.
- 24-1-1933 N Subramanian, (S.), M.A., Mathematics Department, Annamalai  
University, Annamalaiagar P. O., South India.
- 17-4-1931 R Sulaiman, (S.M.), Hon'ble Sir, Chief Justice, High Court, Allahabad.
- 19-3-1931 R Taimini, Iqbal Kishen, Ph.D., Chemistry Department, Allahabad  
University, Allahabad.
- 19-3-1931 R Tewari, Shri Govind, M.A., Mathematics Department, Allahabad  
University, Allahabad.
- 3-4-1933 R Thompson, (C. D.), M. A., Professor of Economics, Allahabad  
University.
- 19-3-1931 R Toshniwal, (G.R.), M.Sc., Physics Department, Allahabad Univer-  
sity, Allahabad.
- 19-3-1931 N\* Vijayaraghavan, (T), D.Phil., Reader, Mathematics Department,  
Dacca University, Ramna, Dacca.
- 1-1-1930 R\* Wali Muhammad, Ch., M.A., Ph.D., I.E.S., Professor of Physics,  
Lucknow University, Lucknow.
- 15-9-1931 R Wall, (W. G. P.), M.Sc., I.E.S., Associate I.E.E., M.R.S.T.,  
Inspector of Schools, Allahabad Division, Allahabad.
- 1-1-1930 N\* Weil, Andre, Docteur ès Sciences, 3, Rue Auguste, Comte, Paris  
(6c), France.

N.B.—The Secretaries will be highly obliged if the members will kindly bring to their notice errors, if there be any, in their titles, degrees, and addresses.



## LIST OF MEMBERS OF THE PUBLICATION COMMITTEES

### Mathematics.

1. Prof. A. C. Banerji, M. A., M. Sc., F. R. A. S., I. E. S., Professor of Mathematics, Allahabad University, Allahabad.
2. Prof. André Weil, Docteur ès Sciences (Paris), 3 Rue Auguste, Comte. Paris (6e) France.

### Physics.

3. Prof. M. N. Saha, F. R. S., D. Sc., Professor of Physics, University of Allahabad, Allahabad.
4. Prof. Ch. Wali Mohammad, M. A., Ph. D., I. E. S., Professor of Physics, Lucknow University, Lucknow.

### Chemistry.

5. Prof. N. R. Dhar, D. Sc., I. E. S., Professor of Chemistry, University of Allahabad, Allahabad.
6. Prof. P. S. MacMahon, B. Sc., M. Sc., Professor of Chemistry, Lucknow University, Lucknow.

### Zoology.

7. Prof. D. R. Bhattacharya, D. Sc., Ph. D., Professor of Zoology, University of Allahabad, Allahabad.
8. Prof. K. N. Bahl, D. Phil., D. Sc., Professor of Zoology, Lucknow University, Lucknow.

### Botany.

9. Prof. B. Sahni, D. Sc., Sc. D., F. L. S., F. A. S. B., Professor of Botany, Lucknow University, Lucknow.
10. Prof. K. C. Mehta, Ph. D., M. Sc., Professor of Botany, Agra College, Agra.

### Mining and Geology.

11. Prof. K. K. Mathur, B. Sc., A. R. S. M., Professor of Geology, Benares Hindu University, Benares.

### Agriculture.

12. Prof. C. Maya Das, M. A., B. Sc., I. A. S., Principal, Agricultural College, Cawnpore.
13. Dr. Sam Higginbottom, Principal, Agricultural Institute, Naini. (Allahabad).

## LIST OF EXCHANGE JOURNALS

| Journals   | Publishers   |
|--|--|
| 1. The Bell System Technical Journal ...                             | The American Telephone and Telegraph Coy., New York, (U.S.A.).               |
| 2. Physics in Meteorology ...  | The Institute of Physics, Exhibition Road, London.                           |
| 3. Proceedings of the Imperial Academy                               | Imperial Academy, Ueno Park, Tokyo, (Japan).                                 |
| 4. Journal of the Franklin Institute ...                             | The Franklin Institute of the State of Pennsylvania, Philadelphia, (U.S.A.). |
| 5. Bell Telephone System. (Technical Publications).                  | The Bell Laboratories, New York, (U.S.A.)                                    |
| 6. Collected Researches ...  | The National Physical Laboratory, Teddington, Middlesex, England.            |
| 7. Proceedings of the Cambridge Philosophical Society.               | The Philosophical Society, Cambridge, England.                               |
| 8. Proceedings of the Royal Society of Edinburgh.                    | The Royal Society of Edinburgh, England.                                     |
| 9. Proceedings of the Indian Association for Cultivation of Science. | The Indian Association for Cultivation of Science, Calcutta.                 |
| 10. Science Notes and Memoirs ...                                    | Indian Meteorological Department, Poona 5.                                   |
| 11. Bulletin of the Patna Science College Philosophical Society.     | The Patna Science College Philosophical Society, Patna.                      |
| 12. Journal of the Indian Institute of Science.                      | The Indian Institute of Science, Bangalore.                                  |
| 13. Current Science ...  | Ditto  |
| 14. Transactions of the Royal Society of Canada.                     | The Royal Society of Canada, Ottawa, Canada.                                 |
| 15. Journal of the Royal Astronomical Society of Canada.             | The Royal Astronomical Society of Canada, Toronto, Canada.                   |
| 16. Publications of the Dominion Astrophysical Observatory.          | The Dominion Astrophysical Observatory, Victoria, Canada.                    |
| 17. Dominion of Canada National Research Council Report.             | Ditto  |

## Journals

## Publishers

- |  |   |
|--|---|
| 18. Proceedings of the Royal Society of Victoria.                    | The Royal Society of Victoria, Melbourne C. I., Australia.            |
| 19. Journal and Proceedings of the Royal Society of New South Wales. | The Royal Society of New South Wales, Sydney, Australia.              |
| 20. Transactions and Proceedings of the New Zealand Institute.       | The New Zealand Institute, Wellington, New Zealand.                   |
| 21. Publications of the Observatory of the University of Michigan.   | The Observatory, University of Michigan, Michigan. (U. S. A.)         |
| 22. Lick Observatory Bulletin  | The Lick Observatory, Mount Hamilton, Berkeley, California, (U.S.A.). |
| 23. Proceedings of the American Academy of Arts and Sciences.        | The American Academy of Arts and Sciences, Boston, (U.S.A.)           |
| 24. Memoirs of the American Academy of Arts and Sciences.            | Ditto   |
| 25. Journal of Mathematics and Physics                               | Massachusetts Institute of Technology, Cambridge, Mass. (U. S. A.)    |
| 26. Year Book 1930   | Academy of Natural Sciences, Philadelphia, (U. S. A.)                 |
| 27. Proceedings of the Academy of Natural Sciences of Philadelphia.  | Ditto   |
| 28. "Bureau of Standards" Journal of Research.                       | Department Commerce, Bureau of Standards, Washington, (U. S. A.).     |
| 29. Contributions from Mount Wilson Observatory.                     | The Mount Wilson Observatory, Pasadena, California, (U. S. A.).       |
| 30. Communications   | Ditto   |
| 31. Annual Report of the Director of the Mount Wilson Observatory.   | Ditto   |
| 32. Anzeiger (Mathematics and Science)                               | Akademie der Wissenschaften, Vienna, Austria.                         |
| 33. Almanach   | Ditto   |
| 34. Anzeiger (Philosophy and History)                                | Ditto   |
| 35. Bulletin de La Classe Des Sciences                               | The Academie Royale de Belgique, Brussels, Belgium.                   |
| 36. Mathematische Und Naturwissenschaftliche Berichte Ana Ungaru.    | Ungarische Akademie der Wissenschaft, Budapest, Hungary.              |
| 37. Sitzungsberichte Der Preussischen Akademie.                      | Preussischen Akademie der Wissenschaften, Berlin, Germany.            |
| 38. Berichte Der Deutschen Chemischen Gesellschaft.                  | Deutsche Chemische Gesellschaft, Berlin, Germany.                     |

| Journals.  | Publishers.  |
|--|--|
| 39. Nachrichten Von der Gesellschaft der Wissenschaften Zu Göttingen.        | Gesellschaft der Wissenschaften Zu Göttingen, Germany.                         |
| 40. Mathematisch-Physikalische Klasse.                                       | Ditto  |
| 41. Geschäftliche Mitteilungen.  | Ditto  |
| 42. Mathematische Naturwissenschaftliche Klasse.                             | Bibliothekar, Heidelberger Akademie der Wissenschaften, Heidelberg, Germany.   |
| 43. Communications from the Physical Laboratory, Leiden.                     | The Physical Laboratory, Leiden, Holland.                                      |
| 44. Science Report of the Tohoku Imperial University.                        | Imperial University of Tohoku, Sendai, Japan.                                  |
| 45. Proceedings of the Physico-Mathematical Society of Japan.                | The Physico-Mathematical Society of Japan, Tokyo, Japan.                       |
| 46. The Keijo Journal of Medicine.   | The Medical Faculty, Keijo Imperial University, Chosen, Japan.                 |
| 47. Journal Du Cycle de Physique et De Chemie.                               | Academie des Sciences D'Ukraine, Kyiv, Ukraine.                                |
| 48. Journal Du Cycle Mathematique.   | Ditto  |
| 49. Bulletin de la classe des Sciences Physique et Mathematiques.            | Ditto  |
| 50. Physikalische Zeitschrift Der Sowjetunion.                               | Physical Journal of the Soviet Union, Kharkov, Chikovsakaya 16, Soviet Russia. |
| 51. Geographical and Biological studies of Anopheles Maculipennis in Sweden. | Kungliga Svenska Vetenskapsakademie, Stockholm, Sweden.                        |
| 52. Kungl. Fysiografiska Sällskapets Forhandlingar.                          | Universitet, Lund, Sweden.   |
| 53. Uppsala Universitets Arsskrift.  | Universitet, Uppsala, Sweden.  |
| 54. Fifty years Retrospect, (Anniversary Volume 1882-1932).                  | The Royal Society of Canada, Ottawa, Canada.                                   |

**LIST OF PAPERS READ BEFORE THE ACADEMY OF SCIENCES  
DURING THE PERIOD APRIL 1932 TO MARCH 1933**

1. On the absorption spectrum of  $\text{SO}_3$ , and heat of dissociation of  $\text{O}_2$  : by Arun Kumar Dutta, M. Sc., Physics Deptt., Allahabad University.
2. On the absorption spectrum of  $\text{N}_2\text{O}$ , and heat of dissociation of  $\text{N}_2$  : by Arun Kumar Dutta, M.Sc., Physics Deptt., Allahabad University, Allahabad.
3. On the Quantitative study of the absorption spectra of  $\text{HBr}$  and  $\text{HI}$  : by Arun Kumar Dutta, M.Sc., Physics Deptt., Allahabad University, Allahabad.
4. On the singularities of Laplace-Abel Integral : by Dr. P. L. Srivastava and S. P. Jain, M. Sc., Mathematics Deptt., Allahabad University, Allahabad.
5. On the phenomenon of after-effect and induction period in the reversible photochemical reduction of Tungstic acid Sol : by Dr. S. Ghosh, D.Sc. and Dr. A. K. Bhattacharya, D.Sc., Chemistry Deptt., Allahabad University, Allahabad.
6. On a generalisation of the second theorem of Bour Baki : by Prof. D.D. Kosambi, Muslim University, Aligarh.
7. On a generalised formulation of Trouton's Law : by Satyendra Nath Ray, M.Sc., Lecturer in Physics, Lucknow University, Lucknow.
8. A Generalisation of a well-known theorem (Vivanti-Borel-Dienes theorem) : by Dr. T. Vijayaraghavan, D. Phil., Reader in Mathematics, Dacca University, Ramna. (Dacca).
9. On the absorption spectrum of some higher oxides : by A. K. Dutt, M. Sc., Physics Deptt., Allahabad University, Allahabad.
10. Post-dissociation radiation from  $\text{SO}_3$  : by A. K. Dutta, M. Sc., Physics Deptt., Allahabad University, Allahabad.
11. Absorption spectrum of Irradiated Iodine : by G. R. Toshniwal, M.Sc. Physics Deptt., Allahabad University, Allahabad.
12. Classification of the spectral lines of  $\text{Cl}_{IV}$  and  $\text{Cl}_V$  : by Suresh Chandra Dev, M. Sc., Physics Deptt., Allahabad University, Allahabad.
13. On two species of the genus *Cephalogonimus* Poirier from water tortoises of Allahabad with remarks on the family Cephalogonimidae Nicoll : by Bindeshri Prasad Pande, M. Sc., Zoology Deptt., Allahabad University, Allahabad.
14. A note on the Expanding Universe : by Prof A. C. Banerji, I. E. S., Professor of Mathematics, Allahabad University, Allahabad.

15. On some experiments with Iodine Vapour : by G. R. Toshniwal, M.Sc., Physics Deptt., Allahabad University, Allahabad.
16. Ageing of ferric phosphate and vanadium pentoxide Sols. at various temperatures: by Dr. S Ghosh, D. Sc., and S. N. Banerji, Chemistry Deptt., Allahabad University, Allahabad.
17. On the absorption spectra of Alkyl Halides: by Prabhat K. Sen Gupta, M. Sc., Physics Deptt., Allahabad University, Allahabad.
18. On the (i) Virtual Independence of the Reverberation period in Architectural Acoustics of the Auditorium Volume, and (ii) its Dependence on sound Frequency.: by Satyendra Nath Ray, M. Sc., Lecturer in Physics, Lucknow University, Lucknow.
19. On the Equation of state of saturated vapour : by Messrs. Brij Bhusan Kak and Sushil Kumar Ghosh, Physics Deptt., Lucknow University, Lucknow.
20. On the relation between energy current incident on an Auditorium Wall and Gauss's Theorem : by Satyendra Nath Ray, M. Sc., Lecturer in Physics, Lucknow University, Lucknow.
21. On the formula for the Locus of discontinuities in the Isothermals of Brombenzol : by Gopal Das Kshetrapal, Physics Deptt., Lucknow University, Lucknow.
22. On some expansions and integrals involving the Parabolic cylinder functions : by V. L. Mutatker, M. Sc., Mathematics Deptt., Allahabad University, Allahabad.
23. Chemical Examination of the Seeds of *Thevetia nerifolia* (Juss), part I.: by Narendra Nath Ghatak, M. Sc., Chemistry Deptt., Allahabad University, Allahabad.
24. On the determination of the Vapour pressure of Zinc Bromide : by M. S. Desai, M. Sc., Physics Deptt., Allahabad University, Allahabad.
25. A note on special theory of Relativity: by Prof. A. C. Banerji, I. E. S., Professor of Mathematics, Allahabad University, Allahabad.
26. Spectra of trebly and quadruply Ionised lead.: by Jai Kishen, Physics Deptt., S. D. College, Lahore.
27. On an Echinostome Cercaria-Cercaria Palustris with notes on its Life-History: by R. C. Chatterjee, M.Sc., Helminthological Institutue, University of Rangoon, Rangoon.
28. On an Experimental Determination of the Law of Variation of the Avogadro's number with Hofmann's Vapour Density apparatus: by Miss A. K. Cheriyan and P. I. Abraham, Lucknow University, Lucknow.
29. An extension of a result in the Factorial Series : by S. P. Jain, M. Sc., Mathematics Deptt., Allahabad University, Allahabad.
30. Chemical examination of the fruits of *Tribulus terrestris*, Linn.: by Narendranath Ghatak, M. Sc., Chemistry Deptt., Allahabad University, Allahabad.

31. Conclusion on the Strength and the Nature of Binding from the continuous absorption spectrum : by Dr. Frank and Dr. Kuhn, Göttingen.
32. An X-ray Investigation of the crystals of Diphenyl Nitrosoamine: by Mata Prasad and S. G. Khubchandani, The Royal Institute of Science, Bombay.
33. Influence of temperature and light intensity on photosynthesis and respiration and an explanation of the phenomena of 'Compensation point' and 'Solarisation' : by Dr. N. R. Dhar, D. Sc., I. E. S., Professor of Chemistry, Allahabad University, Allahabad.
34. Peroxydase from the fruits of *Tribulus terrestris* (Linn). : by Narendranath Ghatak and K. Venkata Giri, M. Sc., Chemistry Deptt., Allahabad University, Allahabad.
35. Normal frequency spectra. : by J. S. Badami, Pundoli Pol, Surat.
36. Absorption spectra of some Halogen derivatives of Methane. : by N. K. Saha, M. Sc, Deptt. of Physics, Allahabad University, Allahabad.
37. A class of Dirichlet's Series possessing essential characteristics of a Taylor's Series. : by Dr. P. L. Srivastava, M. A., D. Phil., Reader in Mathematics, Allahabad University, Allahabad.
38. On an infinite series of integrals involving Sturm-Liouville Eigen functions. : by Dr M. Raziuddin Siddiqi, M. A. (Cantab), Ph. D. (Leipzig), Deptt. of Mathematics, Osmania University College, Hyderabad, Deccan.
39. On the maximum modulus principle. : by Dr. P. L. Srivastava, M. A., D. Phil., and S. P. Jain, M Sc., Mathematics Deptt., Allahabad University, Allahabad.
40. New Blood-flukes of the family Spirorchidae Stunkard from North Indian Fresh-water Tortoises, by Dr H. R Mehra, Ph. D, Reader, Zoology Deptt, Allahabad University, Allahabad
41. Studies on the effect of phosphates on the respiration of green leaves in (1) *Allium tuberosum* (2) *Eugenia jambolana*. : by U. N Chatterjee, M. Sc., Botany Deptt., Allahabad University, Allahabad.

## JOURNALS SUBSCRIBED BY THE ACADEMY OF SCIENCES, U. P. DURING THE YEAR 1932

### PHYSICS

1. Die Naturwissenschaften. (Berlin) 20. Jahrgang.
2. Zeitschrift für Astrophysik. Band 5.

*Financial Statement from 1st January to 31st December, 1932.*

| Receipts.   |            | Expenditure.  |            |
|---|------------|---|------------|
|   | Rs. as. p. |   | Rs. as. p. |
| Opening balance on 1st January 1932.  | 13 11 6    | Establishment   | 622 7 9    |
| Bank balance on 1st January 1932.   | 2,351 8 0  | Contingency. (Including printing, stamps and stationery). | 365 0 0    |
| Government Grant (Non-recurring).   | 2,000 0 0  | Bank Charges on outstation cheques                        | 4 12 0     |
| <i>Membership Fee :—</i>  |            | Journals for 1931   | 63 12 6    |
| Resident membership fee. Rs. 710/.  |            | Binding of journal  | 3 8 0      |
| Non-resident " " 145/   |            | Printing of Bulletin for 1931                             | 1,293 4 6  |
| Part payment of " subscription  |            | Printing of Bulletin Vol. 2, No. 1, 1932                  | 369 0 0    |
| for 1932 ... 5/   |            | One Duplicator machine                                    | 168 0 0    |
| Resident membership fee 1933. 15/   | 875 0 0    | Cash in hand  | 8 12 3     |
| Advertisement charges in the Bulletin Vol. 1, 1931-32 ...                                       | 15 0 0     | Building Fund Rs. 66/                                     |            |
| Building Fund Donation ...  | 66 0 0     | **Balance in Bank Rs. 2,359/0/6...                        |            |
| Receipt of postage stamps transferred from postage account register on 31st December, 1932. ... | 2 5 3      | <i>Bank balance :—</i>                                    | 2,425 0 6  |
| Total Rupees  | 5,323 8 9  | Total Rupees  | 5,323 8 9  |

|   | Rs. as. p. |
|---|------------|
| **Printing charges of Bulletin Vol. 2, Nos. 2, 3 and 4. | 1,015 0 0  |
| Binding of journals.                                    | 96 8 0     |
| Journals.   | 650 0 0    |
| Contingency.  | 165 0 0    |
| Furniture.  | 45 0 0     |
| Balance.  | 387 8 6    |
|   | 2,359 0 6  |

D. R. BHATTACHARYA, D.Sc., Ph. D., F. Z. S.  
*Hony. Treasurer.*

The Academy of Sciences of the United Provinces of Agra and Oudh.



## PRESIDENT'S ADDRESS

ADDRESS OF THE PRESIDENT, PROFESSOR M. N. SAHA, AT THE  
ANNIVERSARY MEETING HELD ON JANUARY 13, 1933.

THE HON'BLE THE MINISTER OF EDUCATION, FELLOWS AND MEMBERS OF THE ACADEMY, LADIES AND GENTLEMEN,—Before rising to address you at the Anniversary Meeting, as President of the Academy, I wish to read to you a message which His Excellency Sir William Malcolm Hailey, the Patron of the Academy, has graciously sent to us on the occasion of the second anniversary, which is as follows:—

**Message from His Excellency Sir W. Malcolm Hailey,  
the Patron of the Academy.**

*I am glad to know that the Academy of Sciences has now safely terminated its second year and is holding its annual meeting on the 13th of January. I am convinced that it is doing good work in co-ordinating scientific effort in this Province, and it performs moreover an important function in bringing before the public the achievements of our scientists. We all hope that a time will come when the Indian public will realise the need for supporting scientific research; apart from other grounds, it would help to gain for India some of the position she hopes to occupy among other nations if she could produce a strong band of scientists whose names were recognized in the great academies of the world. We can only secure public interest in science and scientific workers by some advertisement of their efforts, and it is to my mind quite legitimate that the Academy of Sciences should include this among its activities.*

(Sd.) W. M. Hailey

Governor

United Provinces

9th January, 1933

On your behalf I wish to convey to His Excellency our respectful thanks for these kind words of encouragement. His Excellency's interest and affection for the Academy is well known to the members, and it is a pleasure to find that amidst the burdens of the government he has found time to send us a message of hope and encouragement. We hope that in the years to come we shall be able to render to the community the ideals which he set before us in his last year's address which I again take the liberty of quoting:—"I am confident that in due season you will

see your society occupy an important place in the intellectual life of the Province, originating enquiry, co-ordinating scientific research, and pooling the results."

In this connection I wish to invite the attention of the present audience to another pleasant side of His Excellency's activities, *viz.*, to the great interest he is taking in the industrialisation of these Provinces. You are all aware that, taking advantage of the protective tariff imposed by the Government of India on imported sugar, a large number of factories is being started, and so far these Provinces are fortunately having the lion's share. His Excellency has been taking a most lively interest in the starting of these industries, and he has never refused the request of any party to preside at their inauguration ceremonies. This has stimulated the multiplication of factories, and probably His Excellency's services in this connection will be long gratefully remembered when the country settles down to a calmer mood and derives the full benefit of this industrialisation. The future years promise to be fat years; but in this connection I wish to invite the attention of the industrialists of the very wise counsel given by His Excellency, particularly regarding the advisability of having a co-operative research institute for improving the production and for greater utilisation of the by-products—for, after the fat years, a period of "lean years" is sure to come, when the tariff will be reduced, and competition from other provinces which are now backward in sugar production will be increasingly felt. In these "lean years" which I foresee, adoption of improved methods and utilisation of by-products will enable the factories to tide over the apprehended difficulties. Such research institutes exist in all countries; in this Province they may be organised if the sugar-growers combine and lay aside a small fraction of their income for financing the proposed research association.

My next pleasant duty is to accord a hearty welcome, on your behalf, to the Hon'ble Mr. J. P. Srivastava, M.Sc. Minister of Education in our Provinces and Honorary Fellow of our Academy, who has kindly consented to preside over our annual function. He is an extremely busy man, having to bear the heavy burden of a great administrative department on his shoulders. It was very kind of him to have found time to come to this meeting and encourage us by his presence, guidance, and advice. Himself a graduate in science and an alumnus of the Allahabad University he has been a pioneer and captain of industries in these Provinces, and thus forms a connecting link between science as taught in the universities and its application to the economic life of the country. We expect that he will watch the growth of the Academy in the years to come with loving care and affection.

I am sorry that in the second year of our existence we have to deplore the loss, by death, of two of our most esteemed colleagues. The death of Mr. Nabendu Bhusan Banerji, M.Sc., late of the Indian Railway Service, at the early age of 29, removes from our midst a very promising recruit to the Railways, and a prospective scientific worker. His life was so short that the public had no time to be aware of his great promise. He was a son of the late Dr. Satish Chandra

Banerji, one of the legal luminaries of these Provinces during the last generation. N. B. Banerjee was one of my early batch of students at the Physical Laboratory of the Allahabad University. After a brilliant career in the University he entered, much against his will, the Railway service by open competition. His dislike to the service, as in the case of many other young men of high intellectual capacity was due to his inclination to lead a life of scholarship and of devoted service to science; but, alas! pure science offers so few avenues of existence in our country that a large number of promising young men can exercise no discretion in the choice of their career. Accepting his position with philosophic resignation he tried to apply his scientific training to the elucidation of problems of transport and rates - subjects of national importance in which there are very few experts in this country. He had made considerable progress in this line when his life was cut short by a disease which could not be diagnosed.

In the untimely death of Dr. Dudgeon, at the early age of 46, the Academy has lost one of its most esteemed members, and many of us a personal friend. Dr. Dudgeon was born and educated in America, and was sent to India by the American Mission in 1917 as Professor of Biology in the Ewing Christian College, Allahabad. He made India his home, and became Indian in his sympathies and took a prominent part in the educational life of the country. His contributions to Botany are many and varied; and, as a part-time teacher in the University, he had under him a number of students doing original work in Botany, one of whom was recently awarded the D.Sc. degree. As a mark of recognition of his contributions he was elected President of the Botanical Section of the Science Congress in 1922 and first President of the Indian Botanical Society in 1921. He has been recently on a visit to America, and fell a victim to influenza. The news of his death came as great shock to his numerous friends and admirers at Allahabad, many of whom have been recipients of a Christmas card from him simultaneously with the news of his death. A fuller description of his scientific work will be published later.

We are still an infant body, as we are now entering on the third year of our existence. It will be profitable to recall some of our activities during the last session. Last year we published one *Bulletin* in course of the whole year. This year we are publishing four numbers, of which the first two are already out. You will notice that we have effected considerable improvement in printing and get-up and now our publications rank with the best in the world. Our thanks are due to Dr. S. C. Deb, who has so far looked after the publication of the *Bulletin*. We have also made arrangements that papers published in the *Bulletin* should be regularly abstracted in the Science Abstracts, "Physikalische Berichte," and other abstracts. I am glad to announce that we have been able to exchange our *Bulletin* with publications of most of the learned societies of the world. A full list of such journals is published regularly in the *Bulletin*. In this connection we are extremely grateful to Sir Richard Gregory, the Editor of the *Nature*, who has given a very kindly and sympathetic review of the inaugural ceremony of the Academy in his

well-known journal. Sir Richard Gregory has been a friend of scientists all over the world, particularly to Indian scientists, and I hope he will be accorded a hearty welcome by all scientific workers when he comes to Allahabad, as he has informed me, for a short tour in course of the current month. When he is here I hope we shall be able to convince him of the necessity of having a *Bulletin* for our Society.

Before proceeding to my address I wish to remind you that this is the last year of my Presidentship. I wish to introduce to you my successor, Dr. K. N. Bahl, D.Sc., Professor of Zoology in the Lucknow University. He is a distinguished educationist, and a biologist of great eminence. He has been associated with us in the starting of the Academy from its very embryonic stage, and I hope that under his guidance the Academy will regain fresh vigour and life, and will prove itself more useful to the public. I wish also to express my thanks and my feelings of gratitude to the gentlemen who constituted the council last year. I am particularly indebted to my friends, Professors MacMohan and A. C. Banerjee, for cordial co-operation and hearty assistance. They have given the Academy ungrudgingly their most valued time and service, and, without their loyal co-operation, it would have been impossible to achieve what little we have done.

I now proceed to my address:—

### **The Present Crisis in Dynamics**

In my inaugural address last year I dealt mainly with the value of science to human life. In the present address I wish to deal with a more technical topic, *viz.*, with the present crisis in the science of dynamics. I have chosen this subject for a variety of reasons. As you are all aware the world is now passing through a great crisis. The mid-Victorian period of hope and faith in evolutionary progress has given place to one of distrust and uncertainty regarding the future. The world is not moving onwards, but according to many competent observers it seems to be moving backwards. In his address to the Academy last year His Excellency referred to this spirit of distrust amongst individuals, communities and nations which is leading to the present world-chaos and put to us the query whether science can assist us in securing a more rational manipulation of human passions? As a scientist I would submit the main lesson which science teaches us is that every question should be studied *objectively*, and politics and economics form no exception to this rule. There is, unfortunately in this country, no organisation where data about these questions can be collected and examined dispassionately. On the other hand, these topics are being discussed by different parties in a subjective and almost obscurantist fashion, leading to muddling of issues and production of much heat that can be avoided. However, I do not wish to abuse the prerogative of the politician, and in this gathering of scientific men I would like to discuss a crisis through which the science of physics is passing at the present time. It may interest my political friends who have kindly come here

to know that the science of physics is also passing through a great crisis. As you may be aware, the word physics is derived from a Greek word "physis," which means Nature. The scope of physics is the study of Nature, her phenomena and discovery of the laws behind all these phenomena. These studies are not new, but thousands of years can be recounted which mankind has spent in these studies. The chief task before man has been to increase his experience by making observation and new experiments, and then trying to transfer his results and impressions from the world of perception to his mind, and form a mental picture of the whole process; unless he can perform this task satisfactorily he will have no means of storing his experiences, acquainting his fellow-men with his achievements and transmitting them to posterity. The science of mathematics originated as a short-hand process for recording human experience. But it developed a method, a personality and a life-process of its own, and in its mature growth, it has been found not only useful for recording human experience, but has also very often suggested new paths of knowledge.

A famous writer who is himself a mathematician humorously remarked that the Creator must have been a mathematician. The remark is by no means an exaggeration, though it is safer for scientific men not to indulge in the dubious interpretation of the Divine Will.

### **Ancient Nations had no Dynamics**

To be able to appreciate the present crisis I would ask you to go back over two thousand years, to the old cultural world of the Greek and Hindu savants. One point will at once strike you—The sciences created or inherited by these old people were all static, *e.g.*, geometry, algebra, trigonometry and arithmetic; they had no science to describe motion. Yet we all know that Nature is full of motion. Even phenomena which are apparently static are found on closer scrutiny to consist of latent motion. Witness, for example, the alternation of the day and night all over the world which was a puzzle to ancient people, but which is very simply explained as being due to the rotation of the earth round its axis; or again, take the phenomena of heat, which apparently betray no sign of motion, but science has taught us that it is due to the motion of myriads of molecules which constitute the material body. But though the ancients were conscious of the necessity of having a science of motion, and seemed to have bestowed much thought on it, they encountered immense difficulties in arriving at the correct principles—in fact, it is not much exaggeration to say that they never got anywhere near them: their vague and fruitless speculations are recorded in the problems raised by Zeno the Eleatic over Achilles and the Tortoise, the Stade and the Arrow, and so forth. The chief problem in motion is to define the space-time relationships of particles of matter and compare them with facts of experience. What Zeno meant by his famous paradoxes is

not yet clear. He is supposed, according to some authorities, to have refuted the reality of motion. If that be so, he must be reckoned as one of the greatest humbugs that ever lived. Others claim that Zeno had no such intention; he used the undisputed reality of motion to demonstrate the contradictions which are inherent in our mental picture of space, time and continuity. If this were his intention he must be regarded as a great thinker.

### **Birth of the Science of Dynamics**

Anyhow, the problem made no further progress till Galileo appeared on the scene two thousand years later. This philosopher, when old and almost blind, and deprived of movement by an intolerant clergy within the four walls of a castle which served as his prison, gave us the first solution of the problem of motion. They are now well known to the students of science as the Galileo-Newton laws of motion. Briefly speaking, he gave a precise mathematical meaning to the terms 'mass,' 'force,' 'acceleration,' and 'velocity' which are now used in dynamics, and expressed the relations amongst these quantities in the form of algebraic equations. The invention of infinitesimal calculus shortly afterwards by Newton and Leibnitz provided a very powerful language for expressing these ideas, and for rapidly operating with them—a quality which was lacking in the older algebra.

### **Epistemological Objections to the Galilean Formulation of Dynamics**

It is well known that in the sphere of physics and astronomy the science of dynamics met with all but unlimited success which made it difficult for the ordinary man to appreciate the logical difficulties which were raised to these principles by men like Bishop Berkeley, David Hume and other metaphysicians dealing with the theory of knowledge. They objected to the way in which physicists proposed to transfer events from the world of perception to the physicist's world-picture, and argued that in this process the human mind, which is the chief interpreter, has been altogether ignored, a procedure which Berkeley in particular considered illogical.

Berkeley taught that the qualities ascribed to matter like mass and extension are not inherent in it, but they are largely the creations of the human mind (intellectual constructions); hence they could not represent facts. His arguments, though brilliant, were rather exacting and even old, experienced men could not grasp his idea, and made jests about it. "What is matter? Never mind. What is mind? No matter." Even long after his death Byron lampooned him in these verses:—

When Bishop Berkeley said "there was no matter"  
And proved it—'twas no matter what he said.  
They say his system 'tis vain to batter  
Too subtle for the airiest human head;

And yet, who can believe it? I would shatter  
 Gladly all matters down to stone or lead  
 Or adamant, to find the world a spirit,  
 And wear my head, denying that I wear it.

But Berkeley was wiser than Byron ever thought of him. To-day the idea that in the analysis of the world, the human mind cannot be left out does not appear to be ludicrous.

We find, after all, that the way in which we have ascribed qualities to matter or created our space-time conceptions to represent motion are faulty, tainted by the limitations of the human mind.

### Triumphs of Dynamics

For 350 years mankind has been fascinated by the success of the science of dynamics in interpreting world phenomena, and why should it not be? For the success of dynamics was not only confined to the complete explanation of the mysterious motions of planetary bodies which fascinated the sages of the ancient world—who in these motions saw the hand of Providence writing out Destiny of men and nations, but in course of three centuries subsequent to Newton this science was destined to win fresh laurels in other fields. For physics found that all sensible phenomena by which we derive our conception of the world are in reality resolvable into so many motions of the matter by which it pushes against our senses of perception. Sound is vibration of air-masses, light even a few years back was supposed to be due to vibrations of Aether (it has not yet ceased to be vibrations), heat is resolvable into the chaotic motion of molecules and atoms, and colour depends on the number of vibrations of waves of light affecting our retina. What else is left of the inorganic world? Electricity at once comes into our mind. But physics found at the end of the last century that electricity was more fundamental than matter. In fact, it is now common knowledge that the atoms of matter themselves consist of still more minute atoms of electricity of different signs—the electron and the proton, and the properties ascribed to the atoms by chemists and physicists can largely be traced to the motions of these subatomic constituents.

### Expanding World-Experience

The principles of dynamics were found to be extremely fruitful in these fields, and as a result of their application, the world of perception expanded enormously, and in two directions (1)—in the direction of the larger world of stars, *the greater Cosmos* and (2)—in the direction of the smaller world of atoms—*the smaller Cosmos*. It is exactly the increase of our experience in these two directions which showed that the principles of dynamics possessed the imperfection, which were suspected, though not definitely detected, by the epistemologists.

It is now old story how the astronomer, provided with the telescope and other physical apparatus which have added substantially to his senses, has been going on with his exploration of heavens, *i.e.*, finding out the distance, size, number, and physical characteristics of the universes which we call stars. The methods used in these explorations are not much different from those used by the surveyor in finding out the height or distance of a distant, inaccessible hill. In course of these explorations millions of worlds resembling our solar system and separated from us by enormous distances have been discovered to be existing in the Great Space. It was from a study of phenomena occurring in these distant worlds that scientists first came to the knowledge that light is propagated with finite velocity, a discovery which is of great importance in modern science, for it allowed them to compare the events occurring in these distant worlds with events occurring in this world,—attempts which ultimately led to the discovery of the Theory of Relativity.

### The Principles of Relativity

The main ideas of Einstein's principle of relativity, have now become very familiar, but it is very difficult to appreciate their full import on our classical method of analysing the world-picture. The basis of classical dynamics are three fundamental concepts, *viz.*, that of mass as a property inherent in every piece of matter; the assumption that space can be measured according to the principles laid down by Euclid; the idea of time as a sort of uniform flux. We have already referred to the objections of metaphysicians against these concepts, but have not discussed the nature of the objections. An analysis of Galileo's ideas shows that it is impossible to assure the divisibility of space without bringing in the divisibility of time. The divisibility of length is easily conceived, but what is meant by divisibility of time? Time is one thing with which no experiment was supposed to be possible till Einstein appeared on the scene. But Galileo endowed time with the attribute of infinite divisibility and thus identified duration with extension. In this way, the first steps were taken in converting the science of mechanics into a section of Geometry, but it led to two logical deductions, *viz.*, to the conclusion that Space and Time are of infinite extent. These ideas fitted into the conceptions of Euclidean Geometry. But many old philosophers, notably Descartes, protested against the assumption of an infinite Universe. According to Descartes the extent of the Universe is to be determined by the amount of matter contained in it, and if there were no matter, there would be no space. What Einstein has done is to demonstrate that experimentation with time is also possible and was, in fact, carried out by Michelson and Morley in their famous "Aether-drift" experiment, though the investigators themselves were ignorant of the meaning of their experiment. He found that time and space can no longer be treated as independent of each other, but they enter into a sort of loose connection, making the world of senses four-dimensional, in which we no longer talk of points,



but must talk of events, *i.e.*, points observed at a definite instant of time. The term "distance" ceases to have any logical meaning. Time ceases to be absolute, and, with that, the physicist's dream of making an objective world-picture, independent of the state and motion of the observer, recedes to background. How, under such circumstances, can motion be treated, or can we find substitutes for the law of gravitation, which involves terms like "mass" and "distance," which have now become illogical, and are to be regarded as mere anachronisms.

But Einstein was not a mere iconoclast, he also showed the way for a new reconstruction. He picks up old time-honoured principles, and generalises them according to the new ideas. The corner-stone in his new theory is that mechanics is part of the Geometry of a four-dimensional space-time manifold possessing metrical properties which he identifies with physical characteristics of matter. One interesting result which follows is that he finds that space, and possibly time also, is not infinite, but the extent of the space is conditioned by the amount of mass contained in it, a result which was vaguely foreseen by metaphysicians like Descartes as already mentioned.

Modern astronomical observations have shown that the more distant Nebulæ are receding from us with enormous speed—in fact, the more distant is the Nebulæ, the greater is the speed. This has given rise to the alluring theory of "Expanding Universe" which now forms an entertaining topic for newspaper science. But the world of perception is much larger, and, besides gravitation, very few of the other properties of matter has so far been accounted for by the special theory.

### The Intra-atomic World

All that I have recounted is now old story, and I now turn to the second group of difficulties caused by the emergence of the *quantum* of action, which was first introduced in physics in the year 1900 by Professor Planck of Berlin. It came no bigger than as a mere speck of cloud in the otherwise clear sky of a self-satisfied physics, and was believed by many distinguished physicists as a mere illusion. But it persisted in staying, and, as every physicist now knows, it has proved to be the "*elan vitale*" of the atomic world. The point which I have in mind may be easily illustrated by subjecting Bohr's picture of the atom to a critical analysis. The H-atom in his picture consists of the proton round which the electron revolves in orbits which we may attempt to calculate with the aid of classical mechanics. But there is one important desideratum. We have no means of finding the value of the angular momentum which should be constant. In cases of planetary motion this is obtained from initial conditions, but in the case of the electron it is not possible to subject the atoms of which they form part to direct visual observations. The quantity must, therefore, be guessed. This feat was first accomplished twenty years ago by Niels Bohr of Copenhagen who showed that it must be proportional to Planck's quantum of action because both have the same dimensions; and with some modification the conjecture proved to be highly successful.

The account of Bohr's theory of the H-atom has now passed even into elementary text books, and it has formed the basis of subsequent theories of atomic structure which aim at explaining all the physical and chemical properties assigned to the atom. I wish to speak only of certain logical difficulties in this picture. We find that the electron can revolve only in a certain number of orbits, which can be labelled by the successive integral numbers 1, 2, 3 ... according to the units of angular momentum possessed by the electrons in the different orbits. The question immediately arises: Why are we compelled to limit the orbits to integral numbers? The second point is that the electron, if it is once in a higher, say, the 5th orbit, cannot stay there long but experience tells us that after a period of  $10^{-8}$  sec. or so it comes back to some lower state, the 4th, 3rd, 2nd, or the 1st. But it cannot be precisely stated as to which of these orbits the electron will jump. Experience tells us that the tendency to jump to any orbit is measurable in terms of a definite transition probability for each jump.

### Is the Principle of Causality to be Given Up?

This last circumstance at once brings our picture into definite conflict with the principle of causality which forms the basis of classical dynamics. This principle tells us that for every observed effect there must be a precisely definable cause, which uniquely determines the effect. For example, why does a planet move in a definite orbit round the sun? The cause is that the planet is subject to the law of universal gravitation discovered by Newton, and was observed at a definite instant to move with a definite velocity at a definite distance. These conditions completely determine the *destiny* of the planet. If it is ever found to deviate from the calculated orbit, it must be due to some unknown cause, *e.g.*, the proximity of a third planet. It will be easily perceived that belief in the principle of causality is the very foundation of Modern Science; for if with ancient philosophers we believed that everything is ordained by a Higher Will, no need for scientific study remains. The achievement of the mediæval philosophers consisted in showing that every observable effect can be traced to a cause which is mathematically definable without the intervention of a Divine Will. The labours of scientists have been directed to find out the succession of cause and effect, and has resulted in the lofty structure which we call modern science. It is true in some sciences, *e.g.*, in meteorology the result has not been encouraging, for has not the unreliability of predictions of weather-prophets passed into a by-word? But no scientist has thereby been led to despair in the truth of the law of causality in this field. He finds, with good reason, that the meteorologist, unfortunately for him, has to deal with very complex questions in which infinite variety of factors are present, and he finds it difficult to distinguish between cause and effect. But it is clear that in the atomic problem Bohr had unwittingly violated this principle by making the electron jump spontaneously from one orbit to another. Classical dynamics does not enable us to say why the electron jumps from the 5th orbit to the 4th or the 3rd.

The idea of transition probability is wholly foreign to it. Bohr endowed the electron with a certain amount of *free will* which enables it to determine its destiny in a limited way but apparently without the intervention of any traceable cause.

The position is thus described by Eddington:—"It is a consequence of the quantum theory that physics is no longer pledged to a scheme of deterministic law. Determinism has dropped out altogether in the latest foundations of theoretical physics, and it is open to doubt whether it will be brought back."

### Failure of Classical Dynamics

I have referred to one difficulty, but in fact there are many others. The exploration of the inside of the atom has yielded much new experience which cannot be fitted within our old framework. Though physicists were conscious of the difficulties they were unwilling to speak out their mind until 1925, when Heisenberg, a young German physicist, boldly proclaimed the unpleasant fact. A new pathway must be found to cope with these new facts of experience. Attempts from many directions are being made since 1925, but I do not think that we have as yet come to anything like a final picture. Divested of technicalities these attempts point to a very fundamental departure. The main task of the physicist is to translate events from the world of perception to the physicists' mental picture. In this process the fundamental unit was the particle of matter which was supposed to occupy a Euclidean space-point at a definite instant of time. But a little thinking will show that the mass-point was merely an abstraction, a creation of the human mind, like the geometer's conception of point or line, and in the whole range of his experience the physicist has never been able to discover an actual mass-point. The old atom was long ago shown by Clausius to have finite extensions, but physics did not stop there. The atom resolved itself into a complex of protons and electrons, which are elementary units of positive and negative electricity. But even these cannot be conceived as points, but appear to have extensions of a baffling nature in space which have long been the subject of debate. The abstract particle of matter is now going to be divested of its elementary nature. According to De Broglie, its place is taken by a narrow wave-train possessing a definite amount of energy, which cannot be located at any geometrical point but is spread throughout its own space. Though this idea has received a certain amount of experimental support I must admit that the picture is rather vague and some workers like Heisenberg and Dirac prefer to work with symbols rather than with a definite model, thus avoiding unseen pitfalls.

### The Uncertainty Theorem

In classical dynamics the state of motion of a particle was defined by its location, position and momenta co-ordinates. But if the elementary unit be a wave-packet it is clear that its location in space-time cannot be defined by a Euclidean point plus a point of time, but a certain amount of latitude is allowed. Heisenberg

argues that this uncertainty is inherent in the nature of things themselves and illustrates it by the following example. Suppose we wish to locate an electron accurately in space ; we can only do so by illuminating it with light and putting it under observation under a highly magnifying microscope. But the image produced of a point by a microscope is a small disc plus a series of circular diffraction rings about it. The position is not uniquely determined, but is subject to an uncertainty equal to the radius of the diffraction ring which is  $\lambda/\epsilon$ , where  $\lambda$  is the wavelength of light used and  $\epsilon$  is the angular aperture of the microscope. Hence if we wish to locate the electron sharply,  $\lambda$  should be as small as possible, say, a gamma ray. But in trying to locate the position exactly we have brought a further complication on ourselves, for when the light quantum strikes the electron it tends to impart to it a certain amount of energy, a phenomena on which was discovered by A. H. Compton about a decade ago. The changes in momentum is inversely proportional to  $\lambda$  and  $\epsilon$  and an exact calculation shows that

$$\Delta p \Delta q \sim h$$

where  $h$  is Planck's quantum of action

Thus in any physical measurement, the dynamical co-ordinates of position and momentum become uncertain, and mechanics loses the preciseness which was formerly ascribed to it.

In De Broglie's early picture the particle was replaced by a limited wave-packet and he sought to lay down the principles of new dynamics by a point to point comparison between Hamilton's principle of stationary action which in old dynamics was used for describing the formation of particles, and Fermat's principle of least phase, which describe correctly the propagation of light in space. This attempt was further carried on by Schrödinger.

### Schrodinger's Theory of the H-atom

In Schrödinger's picture, the electron becomes something like a stretched membrane which is capable of possessing a number of definite vibrations fixed by boundary conditions. The vibrations of stretched membranes may be familiar to you, at least every student of physics is familiar with them. A circular membrane vibrates in sections marked out by circles concentric with the centre, and in equal sectors into which the circle can be divided. In Schrödinger's picture, the electron which may be supposed to have been replaced by a three dimensional spherical membrane stretching to infinity, is found to vibrate radially and in zones into which the sphere can be divided. These stand for the different classes of stationary vibrations which are visualized by the orbits made familiar by Bohr and Sommerfeld. The transition from one state to another can be compared to the change of the membrane from one state of vibration to another. No will power on the part of the electron is required. We thus save, to a certain extent, the principle of

causality. But the lynx-eyed critic detected holes even in this otherwise alluring picture.

### **Logical Incompleteness of Schrodinger's Picture**

If a particle of matter can be represented by a wave train, the physicist must demand for a critical examination of the properties of the medium. But the sad experience of Aether, said an emphatic no. A further complication was pointed out by Heisenberg, who showed that the packet cannot hold together for a long time, it must dissolve into nothingness sooner or later. A theory of De Broglie, in which the wave is regarded as something like a ghost whose duty was to pilot the material particle in its career through space-time has also failed, so that the physicists, being tired of drawing pictures which, like modern cinema films, do not last for more than a season, are at the present time taking refuge in symbols. Heisenberg's Matrices, Sixteen Dimensional Geometry, and Weyl's Group Theory, Spinor-analysis, Half vectors and heaven knows what further complications may not be in store. The old-fashioned physicist, who, like an idolater, must have a picture, feels that his days are numbered, and he must give way to the newer generation, imbued with iconoclastic tendencies.

### **The Elementary Mass-Particle**

Apart from these difficulties which, as you see, are caused by the emergence of the quantum of action, we have the space-time difficulties pointed out by Einstein. For a well-defined system of dynamics we must have some objective substitutes for the ideas of time, space, and mass, and a substitute for the old-fashioned mass-particle. It should not be thought that I have given you an exhaustive description of all the difficulties of which we are till now cognisant. The electron and the proton, which are so far known to be the elementary particles, are much more complex than the picture conveyed by a geometrical point. They are found, besides possessing an elementary charge, also definite magnetic moments. To account for this fact, the physicists suppose that they are "spinning."

### **The Mystery Deepens**

But this is only a symbolic way of speaking, and Dirac has shown that all the properties associated with spinning can be deduced if we combine the principles of wave-mechanics with Einstein's theory of special relativity. But so enormous is the mass of operations piled up for this purpose that the inner mechanism is entirely concealed from the view; and one who has the patience to read through the paper is left with the impression that a gigantic machinery has been set in motion to crack a nut. And though the nut is apparently cracked, very strange stuff comes out of the interior for which the author was not prepared. For Dirac's theory gives rise to many unfamiliar terms like 'negative mass' and 'free magnetic poles'

which possess strange and weird properties. For example, a pair of negative and positive masses, in spite of the existence of an attractive force between them, will go on chasing each other in space like a pair of ill-humoured ghosts. To some investigators, Einstein's metrical space-time manifold is like a magician's hat out of which every conceivable surprise is possible. For example, Eddington thinks that the radius of the electron is determined by the radius of the Einstein-Universe divided by the square root of the number of protons in the universe. When I read this paper, I had a feeling that we are returning to the world of the ancients, when it was supposed that man's destiny in space-time was determined by the position of planets and stars in the heavens. We have a bewildering mass of speculations rife now, and the unfortunate reader feels like a Columbus cruising in the uncertain waters of the Atlantic. The solid land is yet to come.

### **Wanted a Mathematical Messiah**

Now I wish to finish. On account of the limitation of the time at my disposal I have not been able to give more than a few snap-shots of the multifarious problems now agitating the mind of the physicist. As you have seen, his world of perception has expanded so enormously (on account of multiplication of workers, and invention of apparatus which have added to his senses) that he is for the moment unable to translate his impressions to his mental picture. The physicist is looking forward to the appearance of a Mathematical Messiah to help him out of his troubles. To the general public, and to those not initiated into the mysteries of this abstruse science, the mathematician is a queer creature, working out phantasies with magic symbols. But occasions have been known when delightful surprises have come from this quarter. Here are a few samples in the words of a critical writer:

"The conic sections, invented in an attempt to solve the problem of doubling the altar of an oracle, ended by becoming the orbits followed by the planets in their courses about the sun. The imaginary magnitudes invented by Cardan and Bombelli describe in some strange way the characteristic features of alternating currents. The absolute differential calculus, which originated as a phantasy of Riemann, became the mathematical vehicle for the theory of Relativity. And the matrices which were a complete abstraction in the days of Cayley and Sylvester appear admirably adapted to the exotic situation exhibited by the quantum theory of the atom." (Tobias Dantzig: *Number, the Language of Science*.)

But at the present time the Messiah is not yet in sight, and the physicist, uncontrolled by any sobering influence, finds himself dazed by his own discoveries and unable to interpret his results. But let us hope, as time goes on, we shall have more and more light regarding the mysterious Universe!

## **SPEECH BY THE HON'BLE MR. J. P. SRIVASTAVA**

EDUCATION MINISTER OF THE UNITED PROVINCES OF AGRA AND OUDH  
AT THE ANNUAL MEETING OF THE ACADEMY OF SCIENCES,  
ALLAHABAD, JANUARY 13, 1933.

DR. SAHA, LADIES AND GENTLEMEN,

I feel it to be a great honour to preside over this meeting here, but I feel a great diffidence because I am undertaking a task in which a brilliant lead was taken last year by so distinguished a person as His Excellency Sir Malcolm Hailey. I am very glad, indeed, to note that within a short period the U. P. Academy of Sciences has attained this position. It has established for itself a name not only in this country, but also in Europe and the Western countries. This result is largely due to the personality of the people behind it. You have in your president a very distinguished scientist—(cheers)—whose name is a household word all the world over. He has made various contributions to science which have been appreciated by everybody. Dr. Saha is correct in saying that His Excellency the Governor has taken a keen interest in this Academy. In fact we are only sorry that we have not been able to be of greater benefit to the Academy. I know you want more money, but money has been scarce, and if we have not been able to give <sup>up</sup> to your expectations, this is not due to any lack of appreciation on our part—we would have done more if we could.

### **No Last Word**

I am not going to enter into the intricacies of Dr. Saha's address this afternoon. He has taken you through a maze of things which has left us all bewildered. There seems to be one thing certain that there is no last word in science, the domain of science seems to be too littered with ideas to be gone into fully, and what is to come next we do not know. The development of scientific research in India is of recent date but I think we have taken a great stride. The award of the Nobel Prize to an Indian scientist is a recognition of the first order and your own achievements here will tell you that you are not lagging behind. If you go through the Bulletin of the Academy you will find that the contributions you have been making to scientific knowledge have been very great indeed. In his speech last year Dr. Saha struck rather a plaintive note and said that science has not received the recognition that it should. It is often said that the average man suffers from lack of ideas

and ignorance and so he cannot take a lively interest in scientific research, but I think we should not jump to the conclusion that he is not at all interested in science as he seems to acquiesce in the benefits that accrue to him as a result of the labours of the scientists and desires—if only from a selfish point of view—that science should continue to make progress to give him further benefits. Science, to-day, is of the greatest advantage to this country. Considering the needs of India there is before you, the scientists, a very wide field of public service apart from the efforts that you make to add to the sum-total of your scientific knowledge. That the lead must be given by scientists in this matter is, I believe, realised by all thinking people.

### **Practical Benefits**

We have no doubt that the ordinary man or even the politician of whom you spoke a little deprecatingly—(cheers)—expects only practical benefits from science. This attitude may not appeal to the scientists, but still the man-in-the-street and the general public want science to render some service which will be of practical value to them. We, in India, have a great problem before us; that is, finding jobs for our educated young men. The politician can do something towards this end, but a great deal of help can be given by scientists. You have referred, Mr. President, to the work which it is possible to do for the sugar industry. There are various other lines in which the scientist can render most useful service. We do have a difficult problem, the solution of which rests with the scientists working in cooperation with the politician, if I may say so.

### **Industrialisation**

Your researches could do a lot to improve the pace at which the country is being industrialised. There are numerous industries which could be helped by scientists and I am very glad to say that your Academy of Sciences is not devoting itself wholly to academic research. You are doubtless aware that with the help of Sir C. V. Raman and as a result of the munificence of the late Rao Saheb Dr. Lakshmi Narayan a large sum has been given to industrial research in the Central Provinces. I hope the United Provinces will not lag behind. Similar efforts have to be made all over the country and I am sure public support and private benefactions will be forthcoming.

The result already achieved by the U. P. Academy of Sciences is itself an invitation for such help and I am quite certain that people will not be found wanting in giving support to the Academy in its work.

### **Unemployment**

You are doubtless aware that the U. P. Government have been making some efforts to solve the problem of unemployment of the middle classes. We have just appointed a Committee to go into the question of settling young men on land, the



idea being that young men who have had scientific education would be able to increase the production of land and thereby make a living for themselves. There, again, the scientists could be of great value. I believe Dr. Saha put up a proposition last year for the development of industries and agriculture in the country which deserves careful consideration. His suggestion to my mind is a very good idea, but of course it may not appeal to the pure financier. In this work you will want the combined help of the scientist and the politician and last of all the financier. Times are bad and all governments even the Government of the United Provinces are helpless in the matter of funds. Well, Ladies and Gentlemen, I do not think I need keep you much longer. I wish to thank Dr. Saha for the personal reference he has made about me. I have come to this Vizianagram Hall after twenty-five years, but I find the Hall <sup>the same</sup> as it was. I am very glad now that the band of scientists that you have in this University is doing useful work and I wish to assure you that so far as the Government of the United Provinces is concerned it will not be wanting in giving you whatever help it can. I need not add that I wish the Academy every success and prosperity, and I wish to congratulate it on its new President, Dr Bahl.

### VOTE OF THANKS BY PROF. K. N. BAHL

I am very thankful to the members of the Academy of Sciences for electing me as their President for the year. I am fully conscious of the heavy responsibility imposed upon me, following as I do Dr. Saha, the founder of the Academy. By virtue of his eminent scientific attainments, Dr. Saha has set up a very high standard which it would be difficult for me to approach. But I feel encouraged in my task by the confidence you have reposed in me, and I hope, with your good-will and co-operation, I shall be able to promote the best interests of the Academy during the coming year.

My very first duty as the President of the Academy is a most pleasant one, which is to propose a very hearty vote of thanks to the Hon'ble Minister, Mr. Srivastava, who has taken the trouble of coming over to Allahabad to preside over this function. A very busy person as he undoubtedly is, it is very good of him to have spared the time to attend our annual meeting, this afternoon. Although it is the first time that the Hon'ble Minister has attended a function of the Academy, he has already given proof of his practical sympathy with our aims and objects, as I have no doubt that the annual grants which we get from the Government, are received through his kind help and active support.

I think it is too late in the day to stress the importance of scientific work in the material advancement of our country, and particularly so in the case of our Hon'ble Minister, who has been a man of science himself, and who, as a captain of industry, has made use of the practical applications of science. He realises full well that the money spent on scientific research is a sound investment which is sure to bring a good return.

I shall ask you, ladies and gentlemen, to join with me in according a hearty vote of thanks to the Hon'ble Minister.

### VOTE OF THANKS BY PROF. N. R. DHAR

I have great pleasure in seconding the vote of thanks moved by my friend Dr. Bahl. In our Province we had Journalist Ministers, Lawyer Ministers in charge of education, but we are lucky now to have a Scientist Minister at the head of affairs. We hope that education in general and science in particular, will flourish under his *regime*.

Scientific education is costly no doubt, but it recompenses the community thousandfold by way of improvement in industry and agriculture. We hope that the money spent for the Academy of Sciences will be repaid by the improvement of scientific, industrial, and agricultural education of the Province.

## OBITUARY

### Dr. Winfield Dudgeon

We regret to record the death of Dr. Winfield Dudgeon, Ph. D. on December 26th, 1932 from an attack of influenza in America where he had gone on furlough and was doing research work at the University of Chicago.

He was in charge of the Department of Biology, Ewing Christian College, Allahabad, and was a part-time teacher in the Department of Botany, Allahabad University.

Dr. Dudgeon was born in 1886 and came out to India in 1912 to join the Ewing Christian College while his connection with the University of Allahabad began in 1922. In 1917, he received the Ph. D. degree of the University of Chicago, U.S.A.

Dr. Dudgeon was for years a member of the Botanical Society of America, of the Indian Science Congress, and of the Indian Botanical Society. He served as the first president of the last-named organization in 1921. He also served as President of the Botanical Section of the Indian Science Congress in 1922. He was a member of the American Honorary Scientific Society, "Sigma XI," and of the more specialized honorary botanical society, "Phi Kappa Phi." He was for some time chairman of the committee of courses in Biology of the U. P. Board of Intermediate and High School Education.

He was not only an enthusiastic teacher but a keen researcher. His chief papers were :—

1. Morphology of *Rumex crispus*—1918.
2. A contribution to the Ecology of the Upper Gangetic plain—1920.
3. Succession of Epiphytes in the *Quercus Incana* Forest at Landour, Mussoorie, Western Himalayas—1923.
4. Ecology of Tehri Garwal—1925.

He also published two very useful books :—

- (1) Guide to Intermediate Practical Botany.
- (2) Key to Mussoorie Plants

During the last few years he was engaged in research on mango flowers and he was completing this work in America at the time of his death. He was further preparing a Memoir on the "Forest Plants of Central India."

His death deprives the Ewing Christian College and the Allahabad University of one of the ablest of Indian Botanists, an inspiring teacher of great ability and experience and a devoted investigator of great merit. He is greatly lamented by his students and friends to whom he endeared himself by his liberality and sincerity.